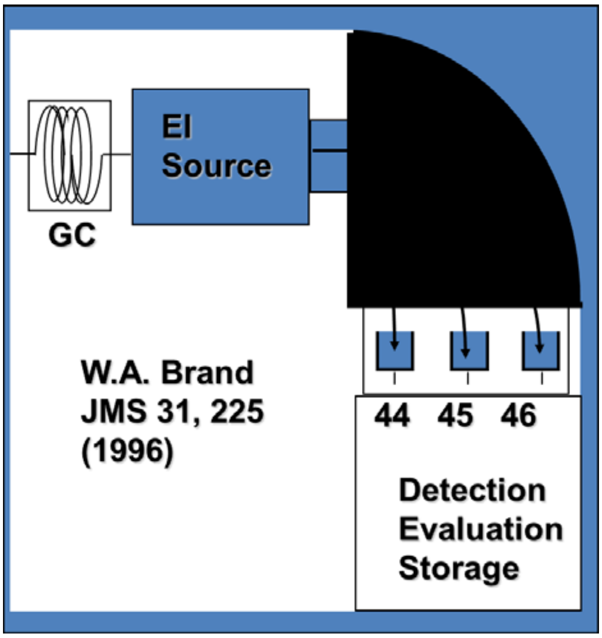
Lecture 1 Introduction, History, Scope and Terminology of Mass Spectrometry

1.1 Topics Not Covered in Detail

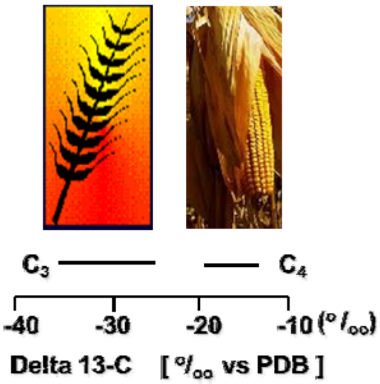
Isotope Ratio MS

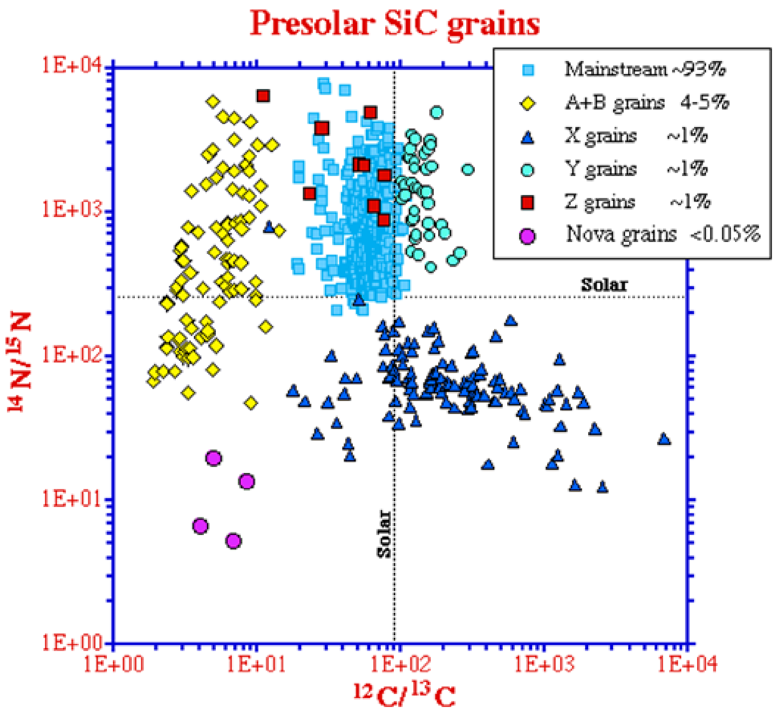


$\delta\ {}^{13}C\ ({}^{o}/_{oo}) = [(R_{Sample} / R_{Standard})-1] \times 10^{3}$

$({}^{o}/_{oo})$ = units of per mil

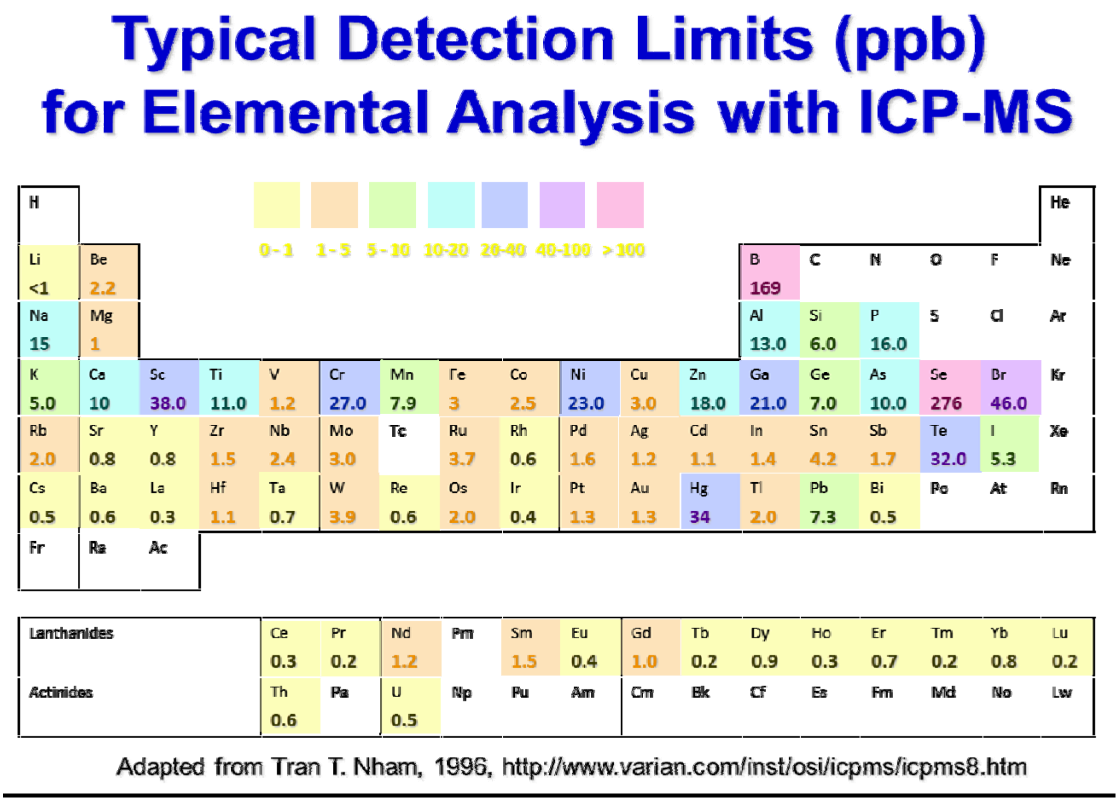
method has a precision of 10 ppm





Inductively Coupled Plasma (ICP) MS

Trace elemental analysis and speciation



Typical Detection Limits (ppb) for Elemental Analysis with ICP-MS

0-1 1-5 5-10 10-20 20-40 40-100 >100

H																	He
Li <1	Be 2.2											B 169	C	N	O	F	Ne
Na 15	Mg 1											Al 13.0	Si 6.0	P 16.0	S	Cl	Ar
K 5.0	Ca 10	Sc 38.0	Ti 11.0	V 1.2	Cr 27.0	Mn 7.9	Fe 3	Co 2.5	Ni 23.0	Cu 3.0	Zn 18.0	Ga 21.0	Ge 7.0	As 10.0	Se 276	Br 46.0	Kr
Rb 2.0	Sr 0.8	Y 0.8	Zr 1.5	Nb 2.4	Mo 3.0	Tc	Ru 3.7	Rh 0.6	Pd 1.6	Ag 1.2	Cd 1.1	In 1.4	Sn 4.2	Sb 1.7	Te 32.0	I 5.3	Xe
Cs 0.5	Ba 0.6	La 0.3	Hf 1.1	Ta 0.7	W 3.9	Re 0.6	Os 2.0	Ir 0.4	Pt 1.3	Au 1.3	Hg 34	Tl 2.0	Pb 7.3	Bi 0.5	Po	At	Rn
Fr	Ra	Ac															

Lanthanides	Ce 0.3	Pr 0.2	Nd 1.2	Pm	Sm 1.5	Eu 0.4	Gd 1.0	Tb 0.2	Dy 0.9	Ho 0.3	Er 0.7	Tm 0.2	Yb 0.8	Lu 0.2
Actinides	Th 0.6	Pa	U 0.5	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lw

Adapted from Tran T. Nham, 1996, http://www.varian.com/inst/osi/icpms/icpms8.htm

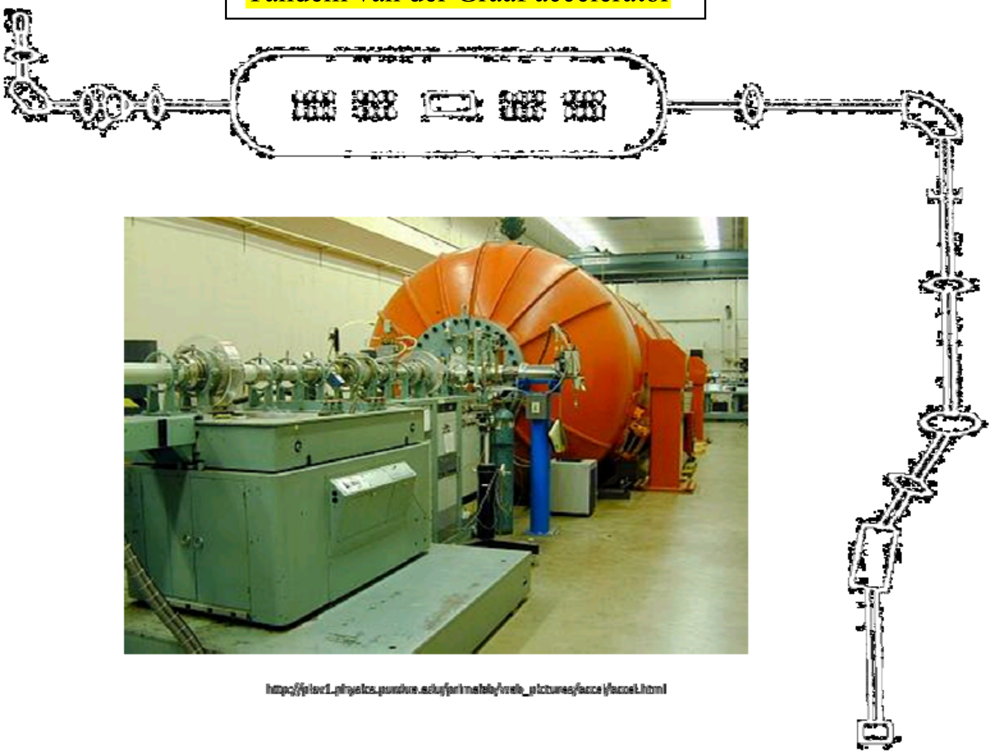
Accelerator Mass Spectrometry (AMS)

Highest dynamic range of all methods: discriminates 1 in 10^{12} minor and adjacent major isotopes

Ion Source:	**5 - 30**	**μA**
Inj. Magnet:	**0.25**	**T**
Accelerator:	**5.9**	**MV**
Anal. Magnet:	**0.73**	**T**
Electro. analyzer:	**78.2**	**kV**
Gas ion. detector:	**83.8**	**Torr**

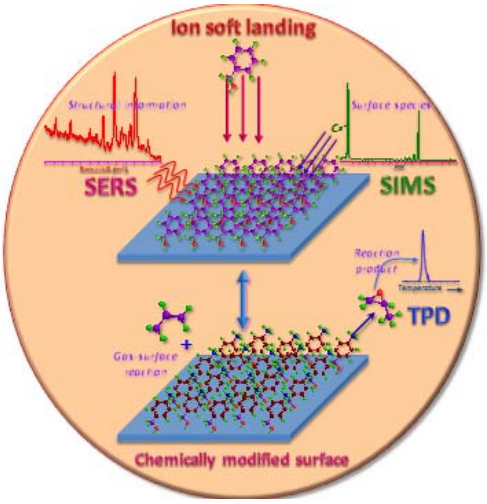
Radio-nuclide	**Detection Limit (10^{-15})**	**Half Life (years)**
^{10}Be	**5**	**1,500,000**
^{14}C	**3**	**5,730**
^{36}Cl	**1**	**301,000**

Tandem van der Graaf accelerator



http://pilsw1.physics.purdue.edu/primelab/web_pictures/accel/accel.html

Surface modification and patterning

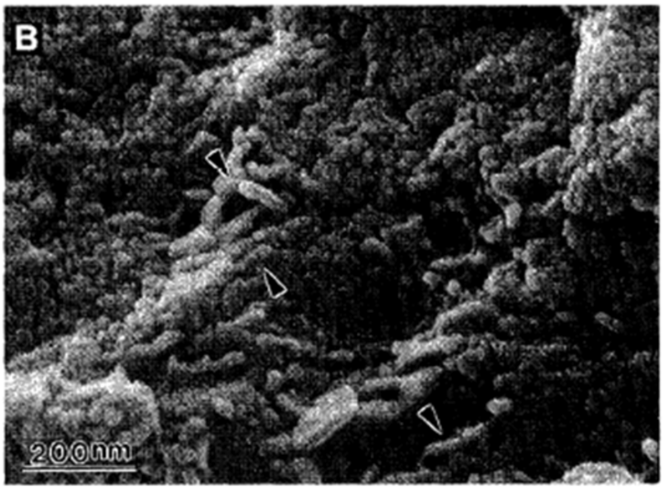


Soft landing ion deposition on surface
SIMS surface ionization method
Reactive landing
TPD – temperature programmed desorption

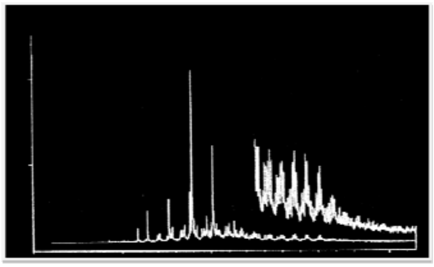
1.2 Some Applications

Materials Analysis:

Meteorite causing excitement about life possibly existing on Mars. This first meteorite found by the Antarctic team in 1984 was initially mis-identified as a diogenite, a rare type of achrondite meteorite. Isotope ratios are consistent with other Martian meteorites but inconsistent with terrestrial values



PAH analysis by laser microprobe MS 40 µm, and detection limits sub-attomole (>10^7 molecules, 1 amol = 10^{-18} mol)

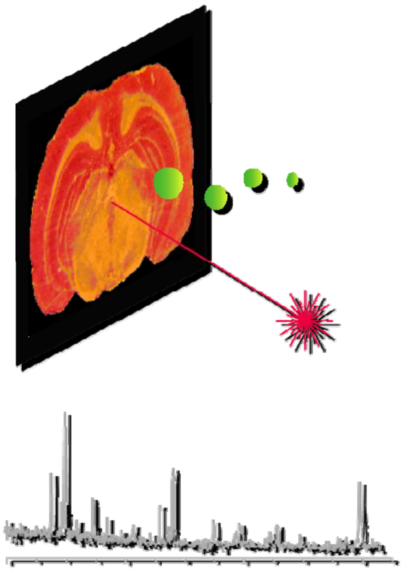


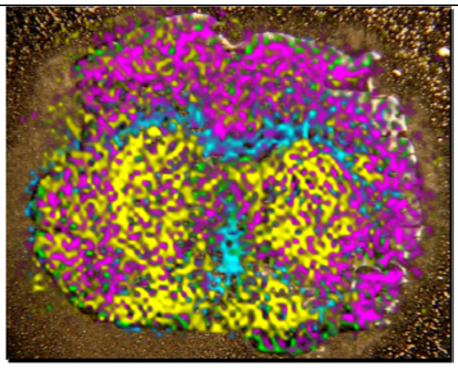
http://www- rator.jsc.nasa.gov/

Applications in biology

Imaging and very high mass

MALDI microanalysis





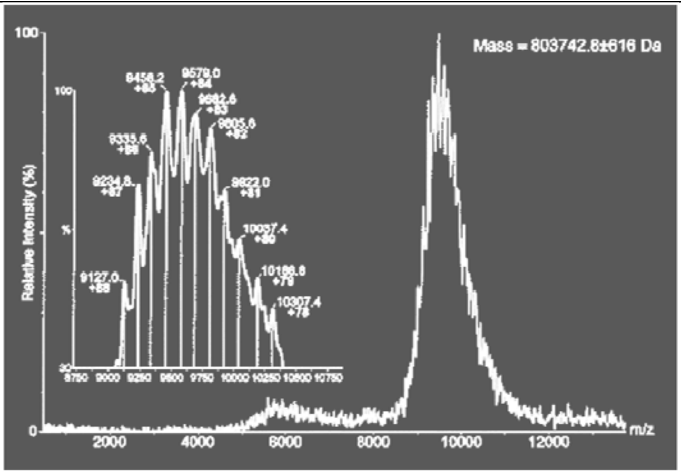
MW 6844

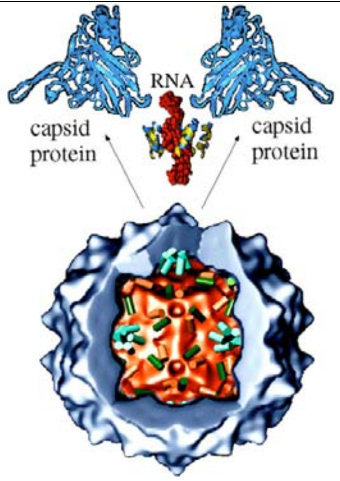
MW 6713

MW 7532

MW 18391

Courtesy from Professor R. Caprioli

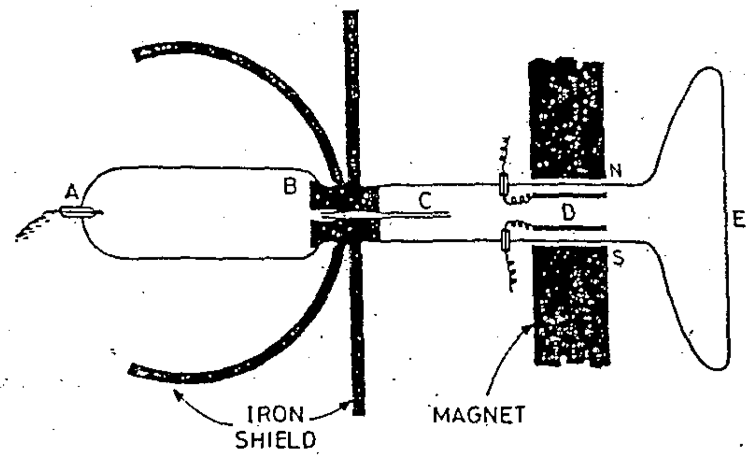




Courtesy Prof. Mark Bier

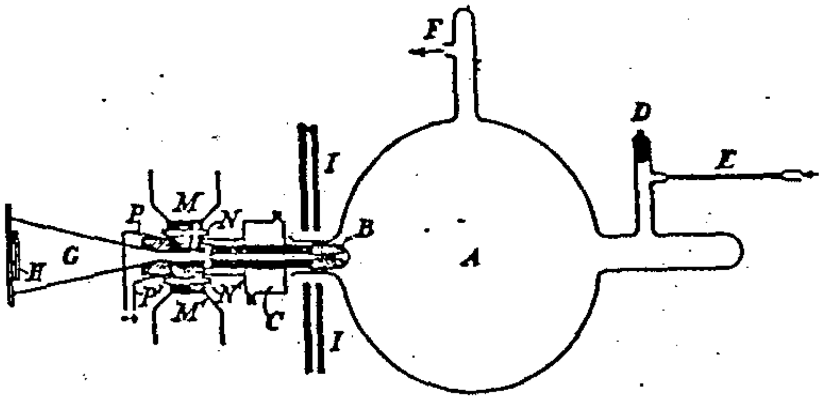
1.3 History of Mass Spectrometry

Thomson and the Positive Ray Apparatus



C. Capillary
B. Cathode
A. Al anode 20 kV
E. Detection (willenite) fluorescence o photoplate
Vacuum using rotary pump
Parallel B, E fields

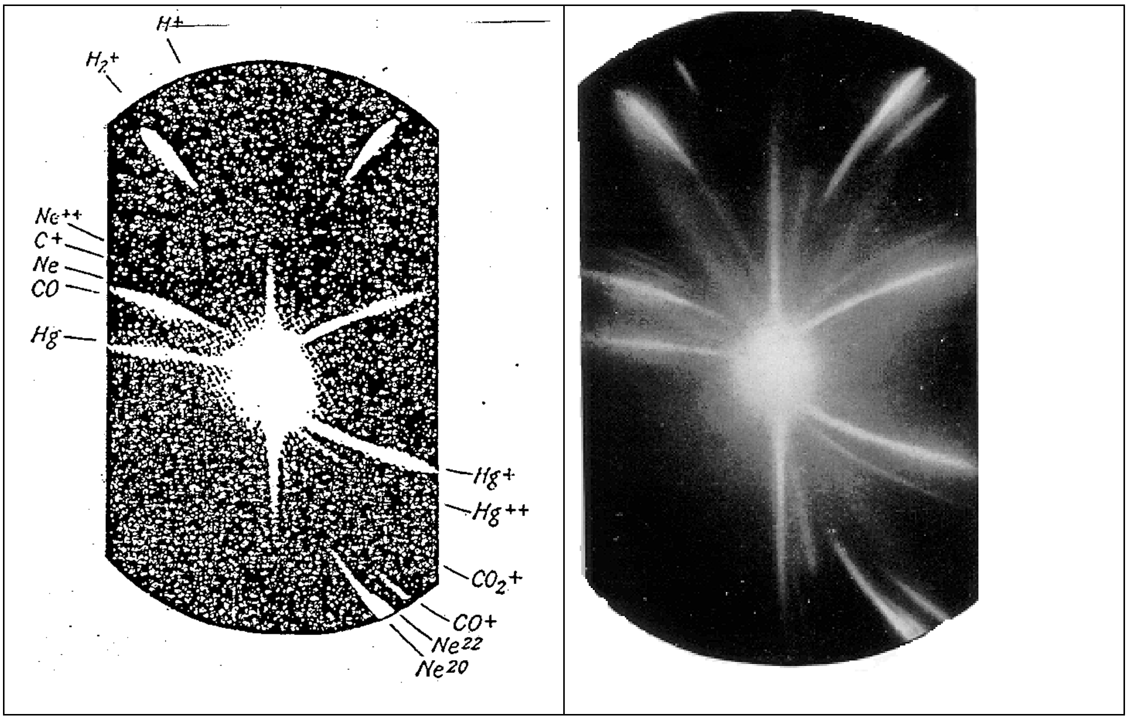
Thomson's parabola apparatus for the study of positive rays. The collimated beam or positive rays issuing from the narrow tube, C, passes through coincident electric and magnetic fields at D



Positive Ray Apparatus
Source, Analyzer, Detection
Thomson's mass spectrograph (parabola instrument) produces e/mv deflections in y direction, e/mv^2 deflections in x direction

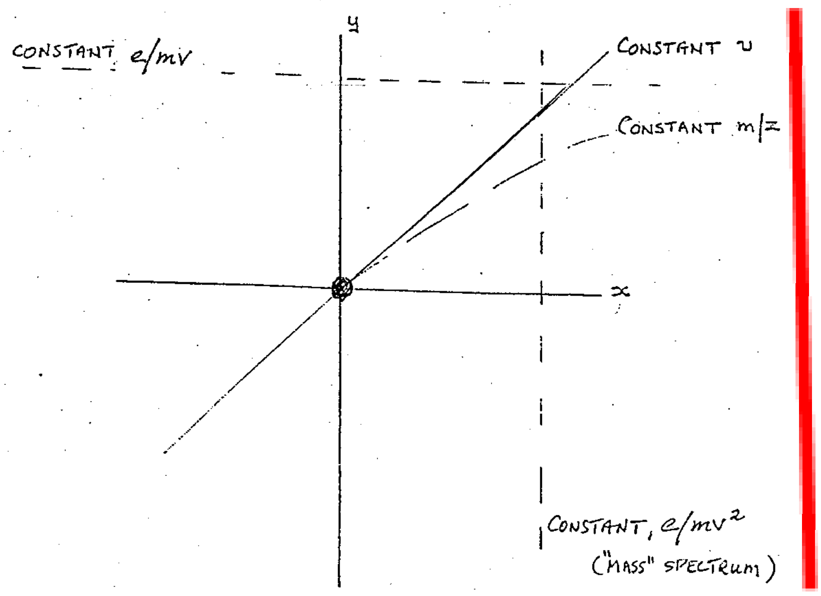
$Bev=mv^2/r$; y deflection $\propto 1/r=Be/mv$
$Ee=mv^2/r$; x deflection $\propto 1/r=Ee/mv^2$

So **parabolas** **B →** **B force ↑** **E → E force →**



Photograph of one of Thomson's photographic plates showing the partial parabola due to the heavy isotope of neon, ^{22}Ne. (Reproduced from "Mass Spectra and Isotopes' by F.W. Aston, by courtesy of Edward Arnold **(Publishers)** Ltd.).

B → B force ↑ E → E force →

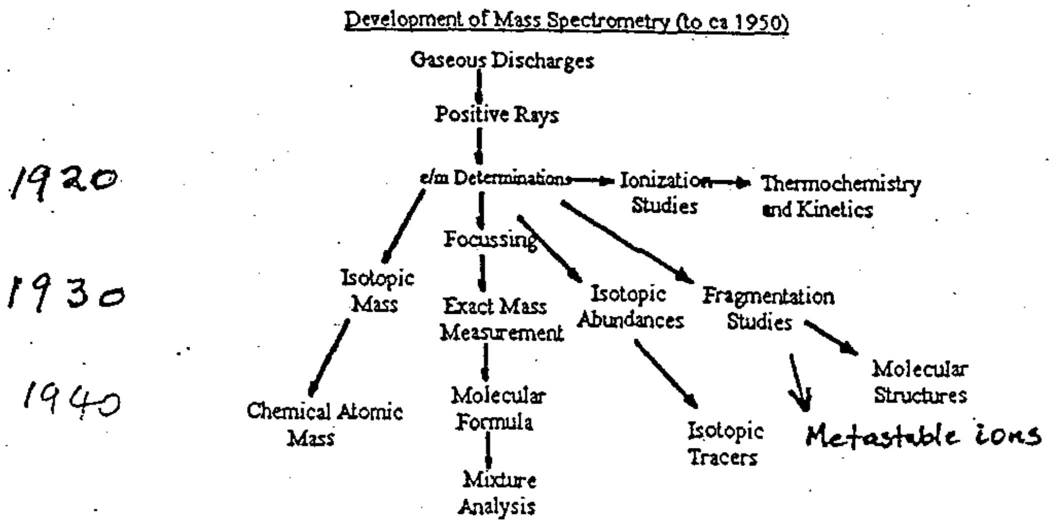


Note absence of focusing

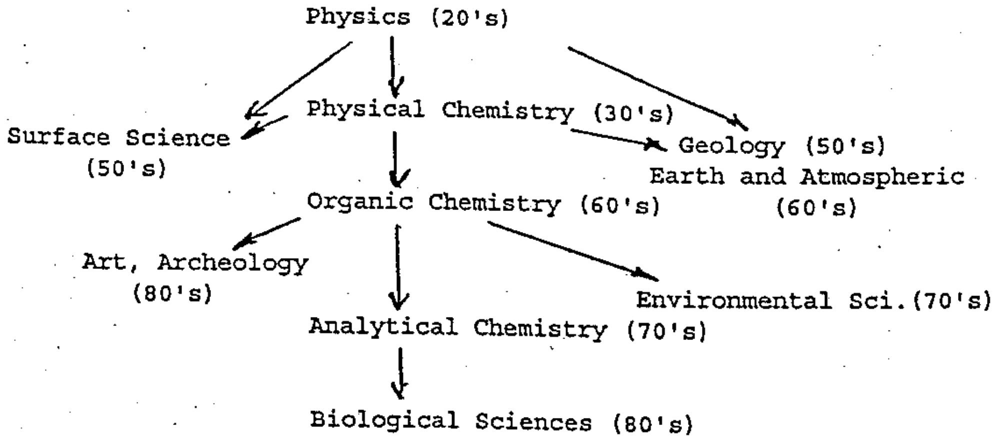
Summary of Historical Developments

Mass spectrometry developed from **19th century physics**
o started with study of electrical discharges in evacuted tubes -Crookes tube
o cathode rays stream from cathode, form shadow of anode when they pass it and hit tube wall and cause fluorescence--Goldstein
o J. J. Thomson discovered the nature of. cathode rays and measured their e/m ratios (cf. modern CR tubes)
o W. Wien discovered the existence of positively charged ions, 1898
o Thomson built an apparatus to study and measure the m/e values of the “corpusules” which make up the positive rays
o Aston demonstrated (1912) the existence of isotopes.
o Instruments capable of high resolution and higher mass measurement accuracy allowed the natural abundance; and the mass defects of the isotopes to be measured.
o Early applications in chemistry included bond energies, ionization energies and other thermochemical determinations.
o 1940, chemical (viz molecular) analysis began (ca. 1940) with the use of mass spectrometric fragmentation patterns to characterize petroleum distillates.

Mass spectrometry development (through 1950):

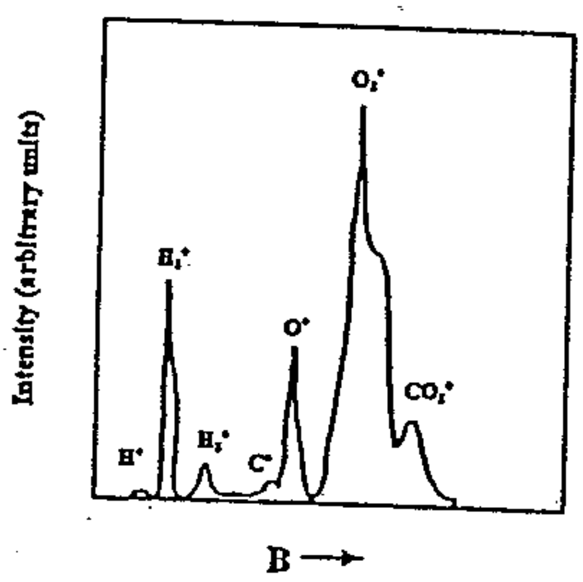


Mass spectrometry has Spread by Discipline as illustrated:



:

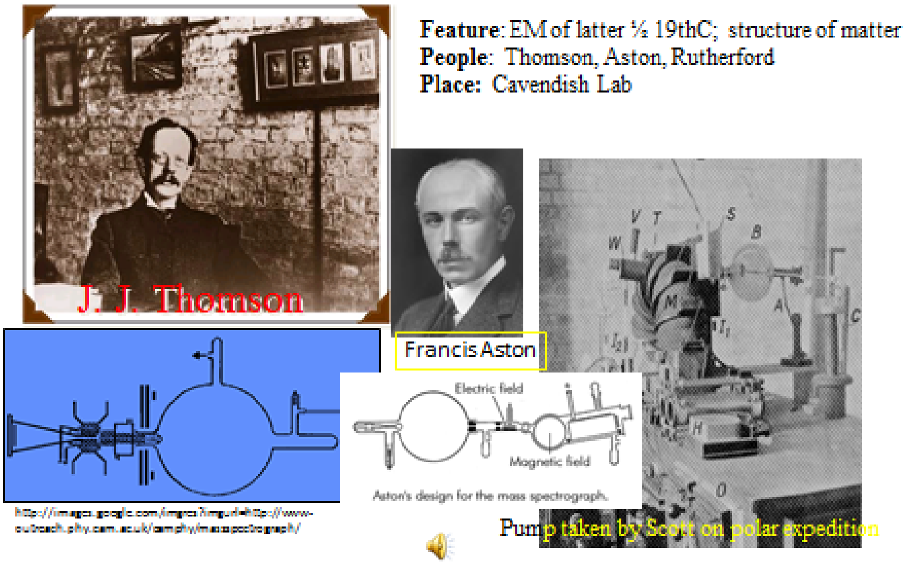
Thomson scanned the magnetic field and used electrical detection to **record the first mass spectra** of which a 1912 example is shown:



Photograph of one of Thomson's photographic plate showing the partially resolved parabola due to the heavy isotope of Neon, ^{23}Ne, together with parabolas for other ions. Thomson, JJ. (1913). Rays of Positive Electricity and Their Applications to Chemical Analysis, London, Longmans, Green & Co., p114

Physics: Early 20th Century

Feature: EM of latter ½ 19thC; structure of matter
People: Thomson, Aston, Rutherford
Place: Cavendish Lab



In summary

Thomson Discovered isotopes, recorded first mass spectra, measured e/m of electron
Thomson observed molecular ions, isotopic ions, multiply charged ions, negatively charged ions, products of charge exchange and other high energy collision processes as well as observing ion/molecule reaction products (eg H_3^+) at low energy. Incipient in Thomson's work was organic analysis, thermochemistry, mixture analysis and collisional dissociation. In 1913 Thomson urged "... especially chemists, to try this method of analysis. I feel sure that there are many problems in Chemistry which could be tad led with far greater ease by this than any other method. The method is surprisingly sensitive - more so than that of Spectrum Analysis, requires infinitismal amounts of material, and does not require this to be specially purified: the technique is not difficult..."

Aston Introduced focusing and measured mass defects of the elements with electrical deflection ("mass spectrograph")

Dempster Used focusing and measured accurate isotopic abundances ("mass spectrometer")

Nier developed the El ion source, double focusing using a combination of sectors for high resolution, and separated and collected 235U. (1930's) In the early 90's he was doing lunar and planetary MS.

Lawrence converted Berkeley cyclotron to a MS, collected 5uA U^+ beams in 1941. A year later 1 mA beams were being made in Calutrons at Oak Ridge -- Instruments that were two stories high and operated in banks, 100 yards long.

Condon of Air Force "blue Book" fame and the Frank-Condon principle,discovered metastable ions (1945), long after collision induced dissociation had been studied by Thomson, Aston and Smythe.

von Ardenne Introduced negative ion MS with has "elektronenanlagerung" experiments in the fifties and sixties.

Washburn was one of the people responsible for the first practical application in chemistry, the analysis of hydrocarbon types in petroleum refining, a method of quantitative analysis which preceded GC (1940). Brewster of this department operated the first such Instrument at Arco, Philadelphia, in 1946.

> The development of commercial “organic” instruments for the high resolution mass spectrometry followed. It was initiated by Beynon. Systematic studies of organic compound fragmentation were begun in the fifties by McLafferty. Applications of mass spectrometry to natural products (alkaloids) begun in the late fifties (Djerassi and Biemann), first biological compounds studied. Intensive, peptides were examined by McLafferty and Biemann soon after this, in the 1960’s.

Some trends in the subject at the moment
1. Biomolecules and higher molecular weight compounds, including non-covalent complexes.
2. Relationship between structures in solution and in the ionic environment
3. Sensitive, precise and universal elemental analysis (ICP and glow discharge MS).
4. Organic reactivity - viz, ion/molecule reactions - under thermalized conditions
5. Laser MS - REMPI, ir based excitation and ionization, etc
6. Proteome and automated sequencing
7. Structures of elusive neutral and ionic species
8. Metal ion chemistry and catalysis
9. Ambient ionization methods

Appendix to Lecture 1: Collected Data & Definitions

Some from ORGANIC STRUCTURALSPECTROSCOPY
JOSEPH B. LAMBERT, Northwestern University
HERBERT F. SHURVELL , Queen's University
DAVID A. LIGHTNER, University of Nevada at Reno
R. GRAHAM COOKS, Purdue University
Prentice Hall, Upper Saddle River, New Jersey 07458

Conversion Factors in Mass Spectrometry

Charge 1 electronic charge = 1.6 x 10^{-19} coulomb
Current 1 ion s^{-1} = 1.60 x 10^{-19}A
Energy 1 eV= 23.06 kcal mol^{-1}; 1 kcal mol^{-1} = 4.18 kJ mol^{-1};
1 eV = 96.4 kJ mol^{-1}
Mass 1 Da =1.66 x 10^{-24} g
Pressure 1 torr = 133 Pascal = 1 mm Hg = 1.33 mbar = 3.2 x10^{19} molecules cm^{-3}
Rate constant
Unimolecular s^{-1}
Bimolecular 1 liter mol^{-1} s^{-1} = 2 x 10-^{21} cm^{-3} $molecule^{-1}$ s^{-1}
Velocity Particle of 1 Da accelerated to 1 eV = 1.1 X 10^{-6}cm s^{-1}

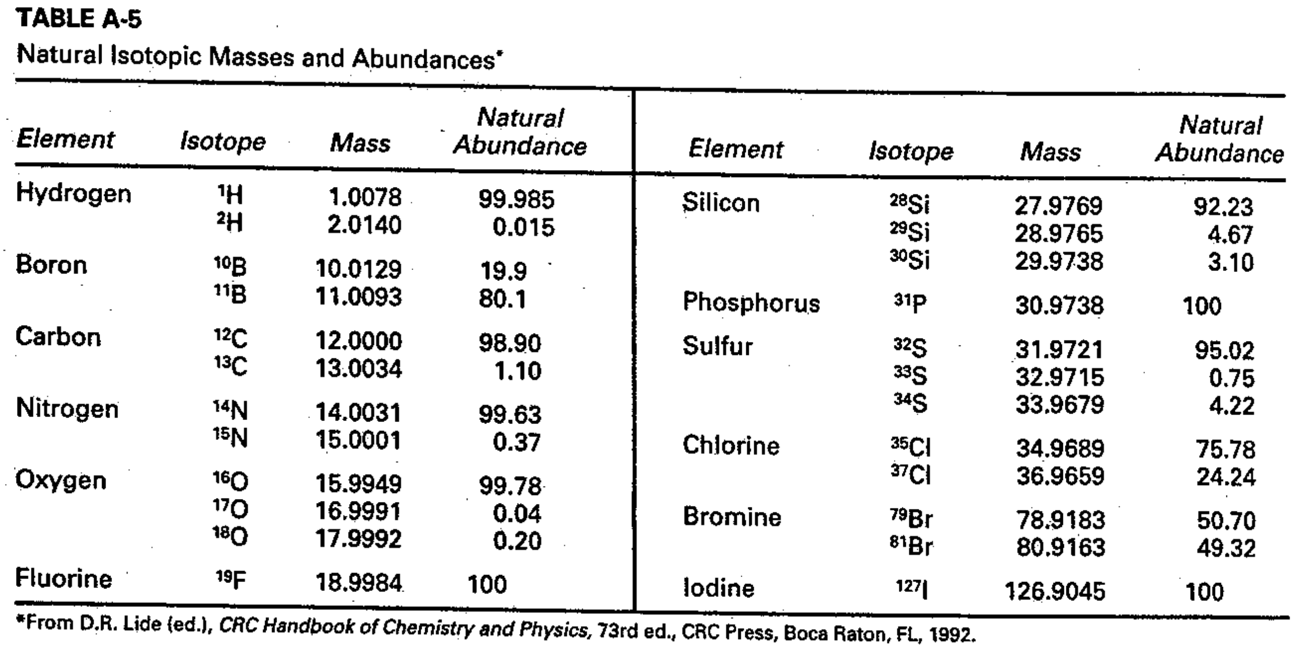


TABLE A-5
Natural Isotopic Masses and Abundances*

Element	*Isotope*	*Mass*	*Natural Abundance*
Hydrogen	^{1}H	1.0078	99.985
	^{2}H	2.0140	0.015
Boron	^{10}B	10.0129	19.9
	^{11}B	11.0093	80.1
Carbon	^{12}C	12.0000	98.90
	^{13}C	13.0034	1.10
Nitrogen	^{14}N	14.0031	99.63
	^{15}N	15.0001	0.37
Oxygen	^{16}O	15.9949	99.78
	^{17}O	16.9991	0.04
	^{18}O	17.9992	0.20
Fluorine	^{19}F	18.9984	100
Silicon	^{28}Si	27.9769	92.23
	^{29}Si	28.9765	4.67
	^{30}Si	29.9738	3.10
Phosphorus	^{31}P	30.9738	100
Sulfur	^{32}S	31.9721	95.02
	^{33}S	32.9715	0.75
	^{34}S	33.9679	4.22
Chlorine	^{35}Cl	34.9689	75.78
	^{37}Cl	36.9659	24.24
Bromine	^{79}Br	78.9183	50.70
	^{81}Br	80.9163	49.32
Iodine	^{127}I	126.9045	100

*From D.R. Lide (ed.), *CRC Handbook of Chemistry and Physics*, 73rd ed., CRC Press, Boca Raton, FL, 1992.

Ionization Modes/Techniques

API	Atmospheric Pressure Ionization
CI	Chemical Ionization
DCI	Direct Chemical Ionization
DESI	Desorption Electrospray Ionization
DI	Desorption Ionization
ECNCI	Electron Capture Negative Chemical Ionization
EH	Electrohydrodynamic Ionization
ES	Electrospray
ESI	Electrospray Ionization
EI	Electron Impact
FAB	Fast Atom Bombardment
FD	Field Desorption
FI	Field Ionization
GD	Glow Discharge
LD	Laser Desorption
MALDI	Matrix-Assisted Laser Desorption Ionization
MPI	Multi-Photon Ionization
NCI	Negative Chemical Ionization
MCI	Negative Ion Chemical Ionization
PD	Plasma Desorption
PI	Photo Ionization
REMPI	Resonance Enhanced Multi-Photon Ionization
SIMS	Secondary Ion Mass Spectrometry
TS(P)	Thermospray
SI	Surface Ionization
SSI	Spark Source Ionization
TI	Thermal Ionization

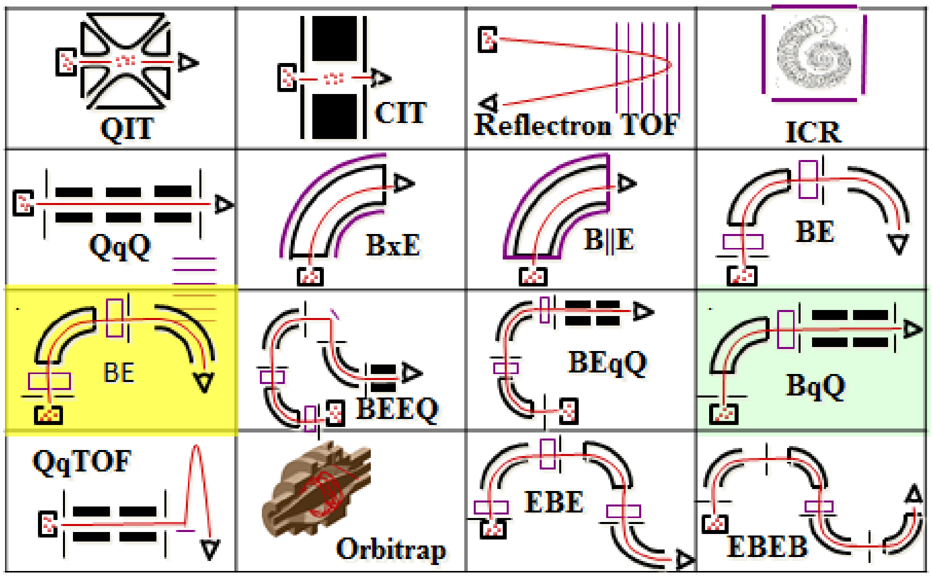
Fields/Analyzers]Instruments

B	Magnetic Sector
E	Electric Sector
ICR	Ion Cyclotron Resonance
Q	Quadrupole
q	Radio Frequency (rf) Only Quadrupole
T	Time
TOF	Time of flight
Trap	Ion Trap
V	Voltage

EB Forward geometry, electric sector followed by magnetic sector, used for double focusing.

BE	Reverse geometry, usually decoupled (ie not used in double focusing mode) to allow for MS/MS, usually MIKES.
BEQQ	A hybrid configuration consisting of a magnetic sector, electric sector, and two quadrupoles.
EBE	Usually a high resolution region followed by los r solution MS/MS.
EBEB or BEBE	A double focusing, double focusing (4 sector) instrument.
FTICR	Fourier Transform Ion Cyclotron Resonance
FTMS	Fourier Transform Mass Spectrometer (same as FTICR)
ITMS	Ion Trap Mass Spectrometer
MIKES	Mass Analyzed Ion Kinetic Energy Spectrometer, BE geometry
TOF	Time of Flight Mass Spectrometer
QQQ	A triple quadrupole mass spectrometer

Variety of Mass Spectrometers: Magnetic & Electric Fields



Scanning Modes

Product Scan	A scan of the product distribution from a single mass precursor. (a.k.a. Daughter Scan)
Parent Scan	A scan of all parents which produce a particular mass ion.
Neutral Gain	A scan of all parents which pick up a particular mass upon collision.
Neutral Loss	A scan of all parents which lose a particular mass.
Linked Scan	A scan with two or more analyzers scanning simultaneously with a fixed relationship.
B/E	Magnet to electric sector ratio is held constant, produces daughter scans in double focusing instruments.

B^2/E	Magnet to electric sector ration is held constant, produces a parent scan.
SIM	Single Ion Monitoring or Selected Ion Monitoring.
SRM	Single Reaction Monitoring or Selected Reaction Monitoring.
MIM	Multiple Ion Monitoring
MRM	Multiple Reaction Monitoring
V	Accelerating voltage scan (used in sector instruments for parent scans)

Collisions/Reactions/Ion Activation Methods

Associative	Collisions leading to product ions of higher mass than reactant ion.
Charge Exchange	A process whereby one particle transfers an electron to another.
Charge Inversion	Usually the removal of 2 e to produce a positive ion from negative ion
Charge Stripping	Production of a **M(m)+** ion from an Mm ion. (Usually the production of a doubly charged positive ion from a singly charged positive ion.)
Dissociative Collision	Collisions leading to product ions of lower mass than reactant ion.
Elastic Collision	A collision in which kinetic energy and internal energy is conserved.
Inelastic Collision	A collision in which kinetic energy and internal energy is not conserved.
Reactive	A subset of inelastic collisions in which a reaction takes place
ARMS	Angle Resolved Mass Spectrometry
CAD	Collisionally Activated Dissociation (CA collisional Activation)
CID	Collision Induced Dissociation
EID	Electron Induced Dissociation
EIEIO	Electron Induced Excitation of Ions from Organics (Same as EID)
ERMS	Energy Resolved Mass Spectrometry
I/M	Ion/Molecule (reaction or collision)
I/S	Ion/Surface (reaction or collision)
NRMS	Neutralization Reionization Mass Spectrometry
PD	Photodissociation or Photo Detachment

Methodology

CE-MS	Capillary Electrophoresis Mass Spectrometry
CZE-MS	Capillary Zone Electrophoresis Mass Spectrometry
FA	Flowing Afterglow
FIK	Field Ionization Kinetics
GC-MS	Gas Chromatography Mass Spectrometry
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
LC-MS	Liquid Chromatography Mass Spectrometry
MIKES	Mass Analyzed Ion Kinetic Energy Spectrometry
MS/MS	Tandem mass spectrometry
MS^n	n stages of mass analysis
PEPICO	Photo Electron Photo Ionization Coincidence
PIPECO	Photo Ionization Photo Electron Coincidence
SFC-MS	Supercritical Fluid Chromatography Mass Spectrometry

General

AMS	Accelerator Mass Spectrometry
APCI	Atmospheric Pressure Chemical Ionization
ATD	Arrival Time Distribution
CI	Chemical Ionization
CID	Collision-Induced Dissociation
CZE/MS	Capillary Zone Electrophoresis/Mass Spectrometry
DI	Desorption Ionization
EA	Electron Affinity
EI	Electron Impact (Ionization)
ES	Electrospray
FAB	Fast Atom Bombardment
FD	Field Desorption
FT-ICR	Fourier Transform Ion Cyclotron Resonance
GC/MS	Gas Chromatography/Mass Spectrometry
GD	Glow Discharge
ICP	Inductively Coupled Plasma
IDMS	Isotope Dilution Mass Spectrometry
IE	Ionization Energy
IRMS	Isotope Ratio Mass Spectrometry
ITR	Integrating Transient Recording
LC/MS	Liquid Chromatography/Mass Spectrometry
LD	Laser Desorption
MAGIC	Monodisperse aerosol generator for introduction from liquid chromatography
MALDI	Matrix Assisted Laser Desorption Ionization
MS/MS	Mass Spectrometry/Mass Spectrometry
MW	Molecular Weight
NCI	Negative Ion Chemical Ionization
PA	Proton Affinity
PD	Plasma Desorption
PIPECO	Photoionization Photoelectron Coincidence Spectroscopy
RBS	Rutherford Backscattering Spectroscopy
RF	Radio Frequency
RIMS	Resonance Ionization Mass Spectrometry
SI	Spray Ionization
SID	Surface Induced Dissociation
SIM	Selected Ion Monitoring
SIMS	Secondary Ion Mass Spectrometry.
TDC	Time-to-digital-converter
TOF	Time-of-flight
TPD	Temperature Programmed Desorption
TS	Thermospray

Definitions

Appearance energy: endothemicity of process: $AB + e^- \rightarrow A^+ + B + 2e^-$

Atmospheric pressure chemical ionization: a variant of chemical ionization performed at atmospheric pressure.

Base peak: the most intense peak in the mass spectrum, hence 100% relative abundance.
Breakdown curve: plot of ion abundance vs. ion internal energy (normalized at each energy); shows mass spectrum as a function of internal energy.
Charge exchange: process whereby one particle transfers an electron to another (such as $M + A^{+\cdot} \rightarrow M^{+\cdot} + A$); used in chemical ionization.
Chemical ionization: method in which neutral molecules are ionized by ion-molecule reactions to generate an ionized form of the molecule at a pressure of about 1 torr. ***Collision-induced dissociation:*** process whereby a mass-selected ion is excited and caused to fragment by collision with a target gas, especially in MS—MS.
Cyclotron motion: cyclic rotation of an ion in a fixed magnetic field.
Desorption ionization: method for ionizing nonvolatile solid samples, in which molecules are subjected to the impact of Energetic particles or photon beams.
Distonic ion: radical ion in which the charge and radical sites are formally located on different atoms in the molecule.
Distribution of internal energy ($P[\varepsilon]$): analogue of Boltzmann distribution for molecules not in thermal equilibrium.
Double focusing: a combination of direction and velocity focusing in sector instruments, used to achieve high resolution. Strictly, the proper term is "second-order double focusing" and it is related to coefficients of the direction and energy terms of the equation of motion for the ions
***Electron affinity**:* enthalpy change for the process: $M^- \rightarrow M + e^-$.
Electron capture**:* ionization process in which a molecule or atom captures a thermal energy electron, typically in a CI source, and generates the molecular radical anion, $M^{-\cdot}$. ***Electron impact: ionization method in which molecules are ionized directly by energetic electrons (usually 70 eV) at low pressure (~10^{-5} torr).
Electrospray ionization: method used to ionize samples from solution by combination of electric field, heat, and pneumatic force.
Even-electron ion: ion with even number of electrons, commonly with a closed-shell electronic configuration.
***Fragmentation pattern**:* set of reactions leading from the molecular ion to fragment ions.
Fragment ion: ion generated by fragmentation not directly by ionization of a neutral molecule.
Gas chromatography—mass spectrometry (GC—MS): combined technique for mixture analysis, in which the separated GC components are passed continuously into the MS. ***Glow discharge:*** method used to ionize solid samples for elemental analysis by applying an electric field to create an energetic plasma.
***Inductively coupled plasma**:* method used to ionize solution samples for elemental analysis by a plasma.
Inelastic collision: collision in which internal energy is not conserved.
Ion internal energy: total electronic, vibrational, and internal rotational energy, referenced to ground state of the ion.
Ion source: device used to generate sample ions by electron impact, chemical ionization, etc.
Ionization energy (IE): minimum energy required to remove an electron from a molecule; endothermicity of the process: $M \rightarrow M^{+\cdot}$.
Isobaric peak (ion): peaks or ions of the same nominal (integral) mass, but different exact mass and composition.
Isotopic peak (ion): peaks or ions due to other isotopes of the same chemical, but different isotopic composition.

Liquid chromatography—mass spectrometry (LC—MS): combined technique for mixture analysis.

Magnetron motion: slow circular drift of an ion along a path of constant electrostatic potential; magnetron motion occurs in ICR as a result of the crossed radial electric field and axial magnetic field.

Mass resolving power: $m/\Delta m$, in which is ionic mass and Δm is the width of the mass peak (typically taken as the full width at half-maximum mass spectral peak height).

Mass spectrum:- Plot of ion abundance vs. mass-to-charge ratio normalized to most abundant ion.

Mass-to-charge ratio (m/z): Daltons/electronic charge.

Mathieu stability diagram: diagram showing the solutions to the Mathieu equation that correspond to stable ion trajectories, displayed as a function of parameters related to operating voltages, mass and charge of the trapped ions.

Matrix-assisted laser desorption ionization: method of ionization that uses laser irradiation of solid analyte present in high dilution in a matrix.

Metastable ion: ion that fragments slowly after emergence from the ion source but before it reaches the detector; in sector instruments, metastable ions give rise to signals that appear at unique *m/z* values related to the parent and product ion masses.

Molecular ion: ion derived from the neutral molecule by loss or gain of an electron or other simple unit, such as $(M+H)^+$, $(M+Cl)^-$, $(M—H)^-$. Ions formed by ESI and MALDI are usually even-electron species such as [M + H] + or [M — H]- and should be referred to as the ‘protonated molecule’ Or ‘deprotonated molecule’ etc.

Molecular mass (Mr):Average molecular mass calculated by using the average atomic mass of the individual elements (e.g. C=12.011; H = 1.008; N =14.007; O=15.999) Chemical average molecular weight.

Monoisotopic molecular mass (Mi): calculated by using the atomic mass of the most abundant isotope of each atom (C=12.00000, H=1.007825, O=15.9949)

Multiply charged ion: ion bearing more than a single charge and having a correspondingly reduced mass-to-charge ratio.

Neutral loss scan: an MS-MS experiment that records all parent ions that lose a particular neutral fragment.

Odd-electron ion: *see* Radical ion.

Parent ion (m_1^+): any ion (including negatively and doubly charged ions) that fragments to product ions.

Parent ion scan: an MS-MS experiment that records all parent ions that produce a particular product ion.

Photodissociation: process in which an ion fragments by absorption of one or more photons

Product ion (m_2^+): ion generated by fragmentation of any parent ion.

Product ion scan: an MS-MS experiment that records all product ions derived from a single parent ion.

Proton affinity: enthalpy change for the process: $MH^+ \rightarrow M + H^+$.

Radical ion (odd-electron ion): charged, open-shell molecule with at least one unpaired electron.

Relative abundance (RA): abundance normalized relative to the base peak.

Resolving power (mass): ability to distinguish between ions differing slightly in mass-to-charge may be characterized by giving the peak width, measured in mass units, expressed as a function of mass, for a specific point on the peak,usually50% or 5% of the maximum peak height

Resolution: 10% valley definition, m/Δm   two peaks of equal height in a mass spectrum at masses m and m-Δm separated by a valley that at its lowest point is just 10% of the height of either peak. Then the resolution (10% valley definition) is m/Δm. It is usually a function of m, and therefore m/Δm should be given for a number of values of m.
Secondary ion mass spectrometry: mass spectrometry based on analysis of particles emitted when a surface, usually a solid although sometimes a liquid, is bombarded by energetic (~ keV) primary particles (such as Ar^+ and Cs^+).
Selected ion monitoring (SIM): experiment in which a mass analyzer is used to detect one or a few ions as a function of time.
Spray ionization: methods used to ionize liquid samples directly by electrical, thermal, and pneumatic energy, by means of a spray of fine droplets.
Surface-induced dissociation: process whereby a mass-selected ion is excited and caused to fragment by collision with a target surface.
Tandem mass spectrometry (MS-MS): two-stage mass analysis experiment; used to study the chemistry of selected ions or individual components in mixtures.
Thermal ionization: method whereby solid samples are ionized on the hot surface of a metal filament.
Unimolecular rate constant ($k[\varepsilon]$): the rate constant k (in s^{-1}) is dependent on the internal energy (ε, always shown explicitly) at which it is measured.

Thermochemistry

AE	Appearance Energy
AP	Appearance Potential
EA	Electron Affinity
IE	Ionization Energy
IP	Ionization Potential
PA	Proton Affinity
GB	Gas Phase Basicity
GA	Gas Phase Acidity (more commonly referred to as $-G_{acid}$)
RE	Recombination Energy
HA	Hydride Affinity

Some Ionization Energies

Element	IE (eV)	Compound	IE (eV)	Compound	IE (eV)
He	24.6	HF	16.0	NH_3	10.2
Ne	21.6	H_2	15.4	$(CH_3)_2C{=}O$	9.7
Ar	15.8	CO_2	13.8	$(C_2H_5)_2O$	9.5
Kr	14.0	CH_4	12.5	NO	9.26
Xe	12.1	H_2O	12.6	Benzene	9.25
H	13.6	O_2	12.1	Pyridine	9.3
C	11.2	C_2H_2	11.4	n-Propylamine	8.8
N	14.5	CH_3OH	10.9	Nitrobenzene	8.7
O	13.6	CH_3CO_2H	10.7	Phenol	8.5
F	17.4	n-Butane	10.5	Aniline	7.7
		H_2S	10.4		

Some Values of Proton Affinites

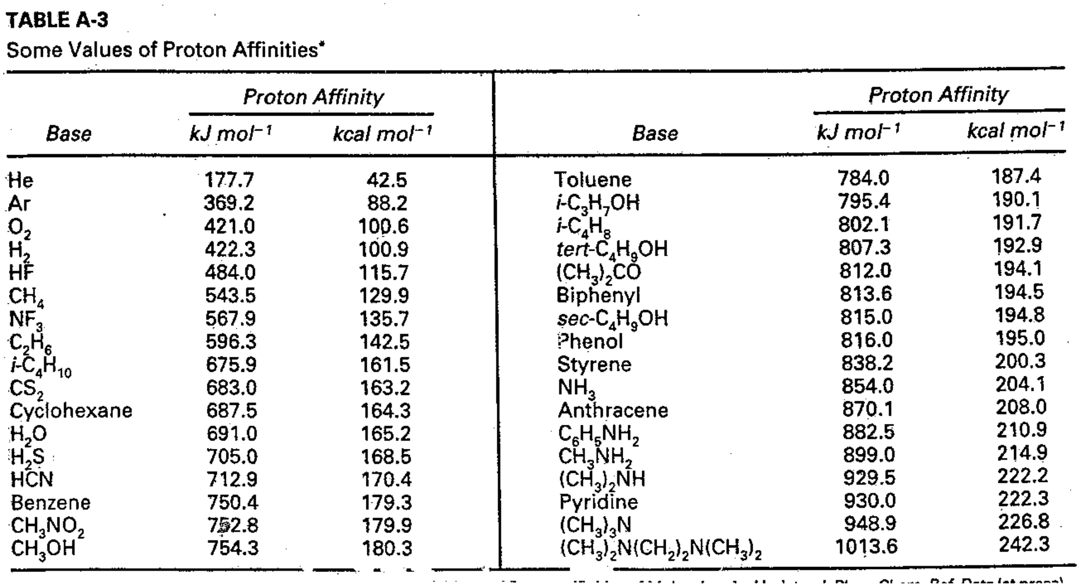


TABLE A-3

Some Values of Proton Affinities*

Base	Proton Affinity *kJ mol⁻¹*	Proton Affinity *kcal mol⁻¹*
He	177.7	42.5
Ar	369.2	88.2
O_2	421.0	100.6
H_2	422.3	100.9
HF	484.0	115.7
CH_4	543.5	129.9
NF_3	567.9	135.7
C_2H_6	596.3	142.5
i-C_4H_{10}	675.9	161.5
CS_2	683.0	163.2
Cyclohexane	687.5	164.3
H_2O	691.0	165.2
H_2S	705.0	168.5
HCN	712.9	170.4
Benzene	750.4	179.3
CH_3NO_2	752.8	179.9
CH_3OH	754.3	180.3
Toluene	784.0	187.4
i-C_3H_7OH	795.4	190.1
i-C_4H_8	802.1	191.7
tert-C_4H_9OH	807.3	192.9
$(CH_3)_2CO$	812.0	194.1
Biphenyl	813.6	194.5
sec-C_4H_9OH	815.0	194.8
Phenol	816.0	195.0
Styrene	838.2	200.3
NH_3	854.0	204.1
Anthracene	870.1	208.0
$C_6H_5NH_2$	882.5	210.9
CH_3NH_2	899.0	214.9
$(CH_3)_2NH$	929.5	222.2
Pyridine	930.0	222.3
$(CH_3)_3N$	948.9	226.8
$(CH_3)_2N(CH_2)_2N(CH_3)_2$	1013.6	242.3

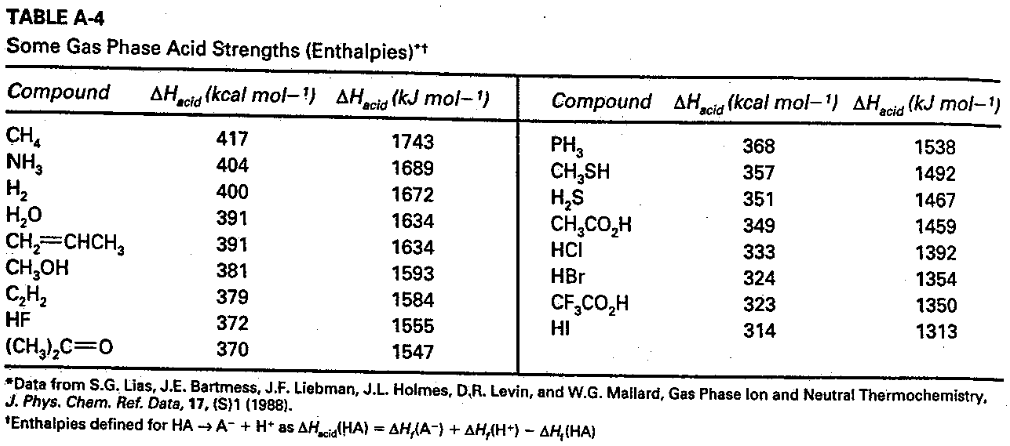


TABLE A-4

Some Gas Phase Acid Strengths (Enthalpies)*†

Compound	ΔH_{acid} *(kcal mol−¹)*	ΔH_{acid} *(kJ mol−¹)*
CH_4	417	1743
NH_3	404	1689
H_2	400	1672
H_2O	391	1634
$CH_2{=}CHCH_3$	391	1634
CH_3OH	381	1593
C_2H_2	379	1584
HF	372	1555
$(CH_3)_2C{=}O$	370	1547
PH_3	368	1538
CH_3SH	357	1492
H_2S	351	1467
CH_3CO_2H	349	1459
HCl	333	1392
HBr	324	1354
CF_3CO_2H	323	1350
HI	314	1313

*Data from S.G. Lias, J.E. Bartmess, J.F. Liebman, J.L. Holmes, D.R. Levin, and W.G. Mallard, Gas Phase Ion and Neutral Thermochemistry, *J. Phys. Chem. Ref. Data,* **17,** (S)1 (1988).

†Enthalpies defined for HA → A⁻ + H⁺ as $\Delta H_{acid}(HA) = \Delta H_f(A^-) + \Delta H_f(H^+) - \Delta H_f(HA)$

GLOSSARY - THERMODYNAMICS

adiabatic

No heat transferred between system and surroundings; for a chemical reaction (ionization, dissociation, etc) this usually means the lowest energy product state is formed (eg. adiabatic dissociation, adiabatic ionization energy).

vertical

Used to describe an electronic transition or ionization (neutralization) occurring at the Born-Oppenheimer limit, i.e., with no change in nuclear coordinates of the molecule (eg. vertical excitation, vertical ionization energy).

ionization energy (IE)

Also ionization energy (IE), sometimes referred to as recombination energy (RE); energy required to remove an electron: M —> M^+ + e; strictly refers to 0 K; may be adiabatic or vertical.

electron affinity (EA)
Energy required to remove an electron from a negative ion: $M^{-\cdot}$ —> M + e; strictly refers to 0 K; may be adiabatic or vertical.

Heat of formation of a positive ion ($\Delta H_f^o(M^+)$)
Sum of the heat of formation of a neutral molecule and its adiabatic ionization potential:
$\Delta H_f^o(M^+) = \Delta H_f^o(M) + IP(K)$ (at 0 K)

Heat of formation of a negative ion **($\Delta H_f^o(M^-)$)**
Difference between the heat of formation of a neutral molecule and its adiabatic electron affinity:
$\Delta H_f^o(M^-) = \Delta H_f^o(M) - EA(M)$

Appearance energy (AE)
Also appearance potential (AP); mass spectrometrically determined amount of energy required to form an ion from a neutral molecule: $AB \rightarrow A^+ + B + e$ or $e + AB \rightarrow A^- + B$

Bond Dissociation Energy
BDE, D[A—B], $D[A^+—B^-]$, etc.
Energy required to break a bond in a molecule; may be homolytic or heterolytic.
D_o^o[A—B] or D_o[A—B] at 0 K $D°_{298}$[A—B] or D_{298}[A—B] at 298K

bond dissociation enthalpy
DH[A—B], DH°[A—B] $DH°_{298}$[A-B], etc.
Enthalpy of homolytic or heterolytic bond cleavage; usually differs from bond energy by RT.

Proton Affinity (PA)
Enthalpy change for the reaction:
$BH^+ \rightarrow B + H^+$; usually pertains to 298K

Gas thase Basicity (GB)
Free energy change for the reaction: $BH^+ \rightarrow B + H^+$

$GB = PA - T\Delta S_{ioniz}$

Gas phase Acidity (ΔG_{acid} or ΔH_{acid})
Free energy or enthalpy change, respectively, for the reaction:
$AH \rightarrow A^- + H^+$; enthalpy change pertains to 298K

$\Delta H_{acid}(AH) = PA(A^-)$; $\Delta G_{acid} = \Delta H_{acid} - T\Delta S_{acid}$
methyl cation affinity (MCA)
Enthalpy change for the reaction:
$BCH_3^+ \rightarrow B + CH_3^+$; usually pertains to 298K

hydride (ion) affinity (HA. HIA)
Enthalpy change (298K) for the reaction
$AH \rightarrow A + H^-$ or $RH \rightarrow R^+ + H^-$