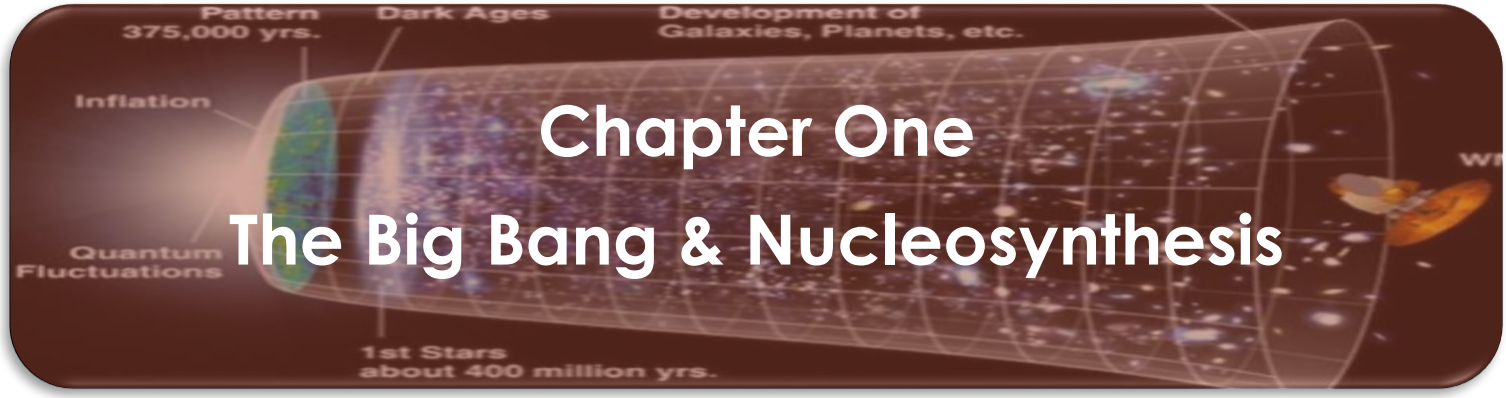
GEOCHEMISTRY

Shaas N Hamdan

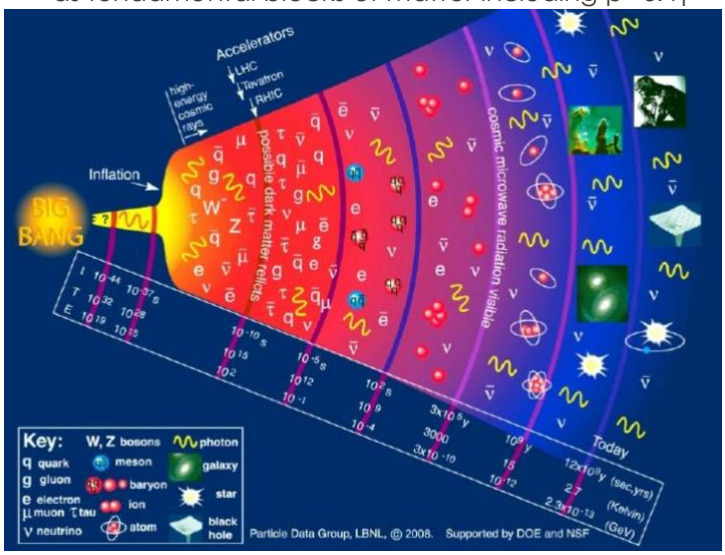


Chapter One
The Big Bang & Nucleosynthesis

- There are 92 naturally occurring element in the Universe (from H to U) formed in the starts by The nuclear fusion & coming to the earth by meteorites

Chronology of the universe	
At the beginning	The universe started like a bubble in stream. formed & expanded rapidly as exploding, From all **matter & energy**
10^{-32} sec	**Quarks** are formed due to high T-P
Later	It expanded & cooled, the quarks combined to form **familiar nuclear particles**, which later became organized into the nuclei of H & He
13.8 sec – 30 min	**Atomic nuclei formation** (T=3x109K). This process did not go beyond the formation of He & it lasted for about 30 minutes
700,000 years	The T dropped to about 3000K, electrons became attached to the atoms of **H & He**
	Matter & energy were then separated from each other & the universe became transparent to light
	the matter organized into stars, galaxies, & galactic clusters as the universe continued to expand to the present time

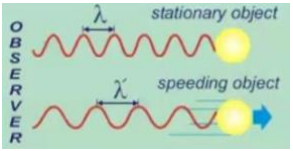
- **Quarks**: subatomic particles & leading candidates as fundamental blocks of matter including p^+ & η

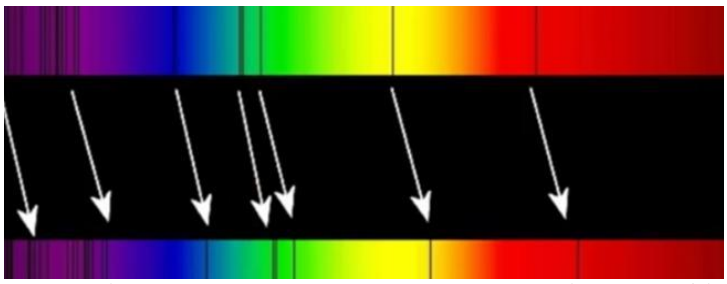


- **Red shift** of the spectral lines due to doppler effect revealed the expanding nature of the universe

Doppler's Equation:

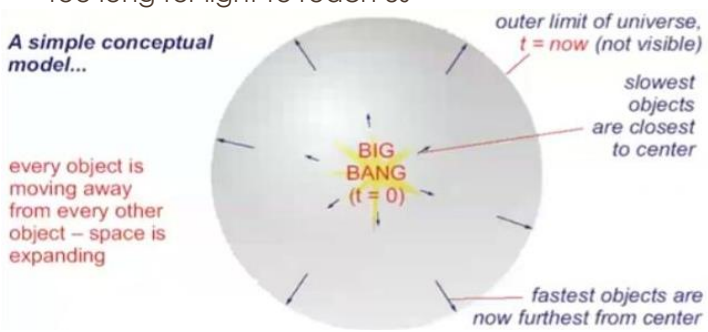
$$\frac{\lambda'}{\lambda} = 1 + \frac{v}{c}$$



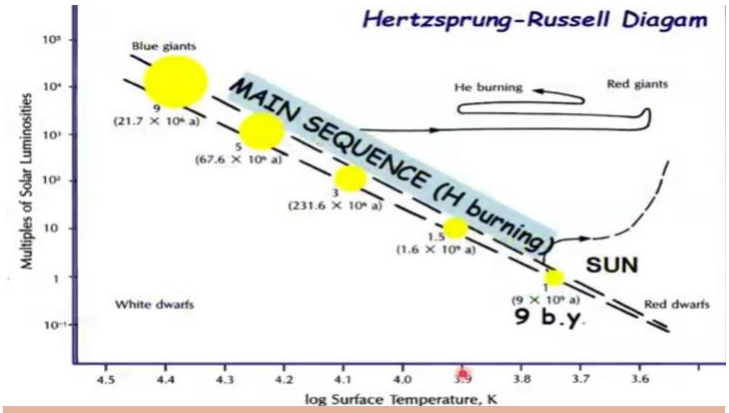


لكل عنصر في الطبيعة خطوط امتصاص باماكن محددة، وعندما يكون الجسم مبتعدا عنا فان خطوط امتصاص العناصر التي يحتويها تنزاح نحو الاحمر واذا كان مقترب تنزاح نحو الازرق، وفي دراستنا للنجوم فقد وجدنا ان خطوط امتصاصها تنزاح نحو الاحمر وهذا يعد دليل على ان النجوم تبتعد عنا وبالتالي دليل ان الكون يتوسع

- **In the future, will the universe end expanding?** If the material contained in the universe will permit gravity to overcome expansion, then it will contract until it disappears, Since it has a beginning & is still expanding, it cannot be infinite in size; edge of the universe cannot seen with a telescope since it takes too long for light to reach us



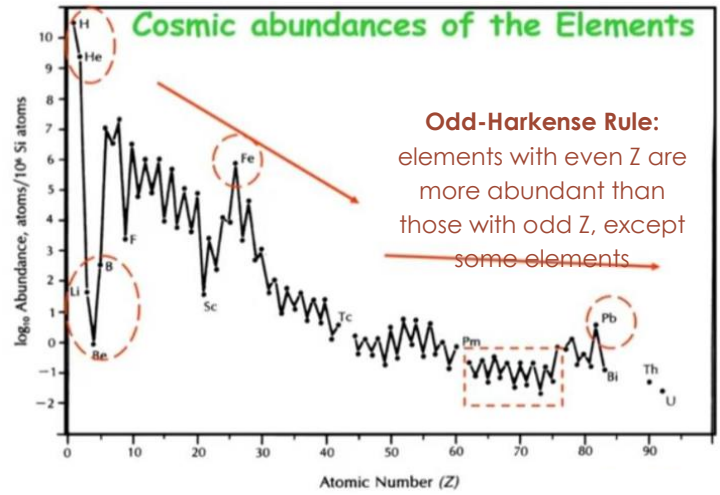
- **The age of the universe** is about 14.5 ± 1.0 Ga
- **Stellar Evolution:** Matter organized into hierarchy of heavenly bodies which listed in order of decreasing size: Clusters, Galaxies, Stars, pulsars, black holes, Planets, Satellites, Comets, Asteroids, Meteoroids, Dusts, Molecules, & Atoms
  - ➢ Billions of stars form a galaxy
  - ➢ large number of galaxies form clusters
- **Stars are the basic units in the universe:** Matter evolve by nuclear reactions in a stars
- **Nebular**: clouds of gas (mainly H & He) & solid particles found in the space between the stars
  - Contract to form stars whose evolution depend on their masses & H/He ratio
  - Evolution of stars described by surface T & luminosity, which proportional to masses
  - Energy production by H burning starts in core of Nebular when the T = $2x10^6$K & a star is born



Hertzsprung-russell diagram

يستخدم لوصف تطور النجوم، تتناسب درجة الحرارة السطحية لأغلب النجوم مع شدة إضاءتها الظاهرية، وكلما زاد حجم النجم تزداد درجة حرارته وشدة اضاءته لان كتلته تزداد فتزداد عمليات الاندماج النووي في قلبه، ومتوسط اعمار النجوم العملاقة قليل لانه يستهلك الكثير من الوقود

عند انتهاء H يبدأ النجم في دمج العناصر الاثقل مثل He فيتحول الى عملاق احمر

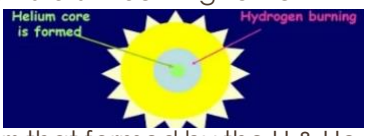


- > 75% of the mass of the universe is H, & >99%H + He
- Elemental abundances drop off **exponentially with increasing Z to 60**, after remain almost **constant**
- Li, Be, & B showed marked depletion to higher & lower Z numbers due to the spallation process
- There is a pronounced peak in vicinity of Fe in addition to other less marked one at higher Z
- 2 elements (technetium, Promethium) don't occur in the solar system, because all their isotopes are unstable & decay rapidly into another elements
- The elements with Z > 83 (Bi) have no stable isotopes & occur at very low abundances
- **Helium Burning:** In 1st-gen stars H burning to He

$^{1}_{1}H + ^{1}_{1}H \rightarrow ^{2}_{1}H + E$

$^{2}_{1}H + ^{1}_{1}H \rightarrow ^{3}_{2}He + E$

$2^{3}_{2}He \rightarrow ^{4}_{2}He + 2^{1}_{1}H + E$



- **First generation stars:** stars that formed by the H & He which formed by the Big-Bang (10Ma), massive stars so stayed for a very short time
- Helium burning takes place in stars having masses of 80% or more of our Sun
- If the conditions are right then He burning is initiated & heavier elements are synthesized

$2^{4}_{2}He \rightarrow ^{8}_{4}Be$ (unstable, $t_{½}$ = 10-16sec)

$3^{4}_{2}He \rightarrow ^{12}_{6}C$ (heavy element, triple a process)

- **Second generation stars:** Formed by H, He, & some heavy elements (to Fe)
  - Our sun is 2nd gen star (contains elements heavier than He such as C, O, N)
  - Heavy elements facilitated burning of H into He
  - Our sun burning H according to the CNO cycle

$^{12}_{6}C + ^{1}_{1}H \rightarrow ^{13}_{7}N$ –decay→ $^{13}_{6}C$

$^{13}_{6}C + ^{1}_{1}H \rightarrow ^{14}_{7}N$

$^{14}_{7}N + ^{1}_{1}H \rightarrow ^{15}_{8}O$ –decay→ $^{15}_{7}N$

$^{15}_{7}N + ^{1}_{1}H \rightarrow ^{12}_{6}C + ^{4}_{2}He$

The differences between 1st gen & 2nd gen. Stars		
	Produced by	Rate of diffusion
1st	H, He	slower
2nd	H, He, + heavy elements	Faster becouse havy element react as catalyst

يكون النجم بحالة توازن بين قوتين (جاذبيته نحو المركز والطاقة النووية بعكس المركز) وعندما يستهلك الهيدروجين تقل القوة الاندماج النووي فينكمش النجم على نفسه وهذا يسبب ضغط وحرارة شديدين في قلب النجم فيبدأ بدمج ذرات أكبر من H مثل He فيترك تتابع main sequence ويصبح red giants ويتمدد expansion ويتوقف الاندماج عند الحديد لان طاقة الربط النووي في نواة الحديد عالية جدا لذا نحتاج ضغوط ودرجات حرارة مهولة جدا، لذا تزداد كمية الحديد وعندما ينفذ كل وقود النجم الاخف من الحديد ينفجر على شكل Supernovae

$^{16}_{8}O + ^{4}_{2}He \rightarrow ^{20}_{10}Ne$..... decay to ^{56}Fe

- **σ (nucleus of He) process**: produced all elements in the stars during main sequence & red giant stages, element heavier than Fe cannot be produced (due to repulsion forces between large & +ve changed nuclei (heavy nucleus), & σ-particles)
- explains the presence of elements with even Z:
  1. Rate of fusion of heavy nucleus < other nucleus
  2. Atomic formed by CNO cycle are even Z, but smaller amount of Odd Z formed by reactions among fusion products:
- In the final throes of red giant stage, a new type of nuclear reaction comes into play, producing a host of heavy nuclei in small abundance (**η-capture**)

$\eta + ^{A}_{Z}X \rightarrow ^{A+1}_{Z}X$ (new heavier nucleus)

$^{56}Fe + \eta \rightarrow ^{57}Fe + \eta \rightarrow ^{58}Fe + \eta \rightarrow ^{59}Fe$ (unstable $t_{½}$ 45d)

  - هذه العملية تكون عناصر أثقل من الحديد
- **β decay** is one process that unstable atoms can use to become more stable (β^{+} & β^{-})
  - تنتج يسبب العناصر الغير مستقرة التي نتجت من اضمحلال النيوترون وهي شحنة سالبة (الكترون)
  - If a nucleus absorbs too many neutrons, it will eventually become too n-rich to be stable & decay by emitting e^{-} this is called **β-decay** (convert n into p & add 1 to the atomic number)

$2^{14}_{6}C$ –β^{-}→ $^{14}_{7}N + e^{-} + \nu'$ (antineutrino)

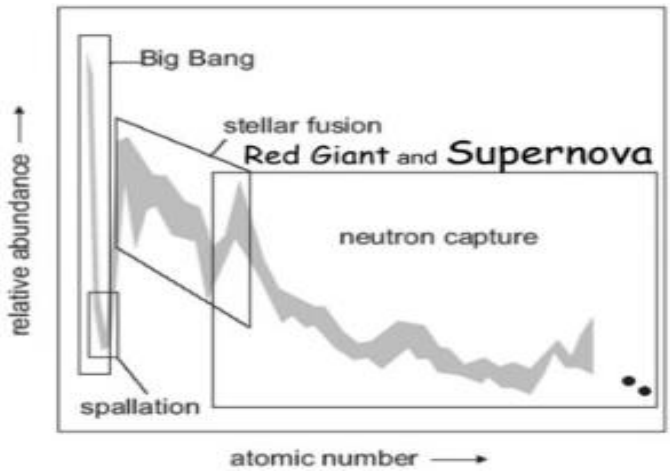
One η from C capture into p + e^{-} + ν'

$^{10}_{6}C$ –β^{+}→ $^{10}_{5}Bo + e^{-} + \nu$ (neutrino)

سبب ندرة العناصر الثقيلة هي انها تكونت في هذه العملية خلال عملية ال Supernovae وهي مرحلة قصيرة جدا ما يفسر ندرة هذه العناصر

- Types of neutron-capture processes (account for synthesis of all elements with Z > Fe)

Process	Neutron flux	During
s-process	Moderate	Late red-giant stage
r-process	High	In supernovae



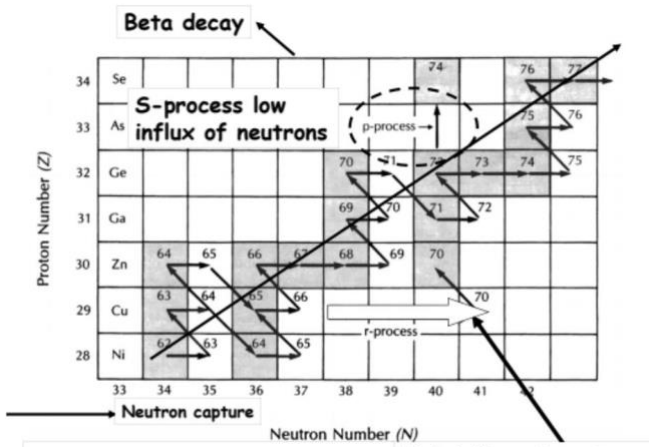
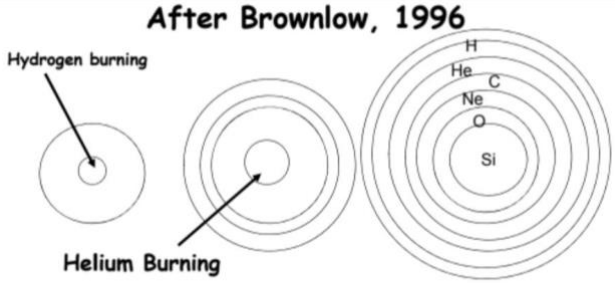


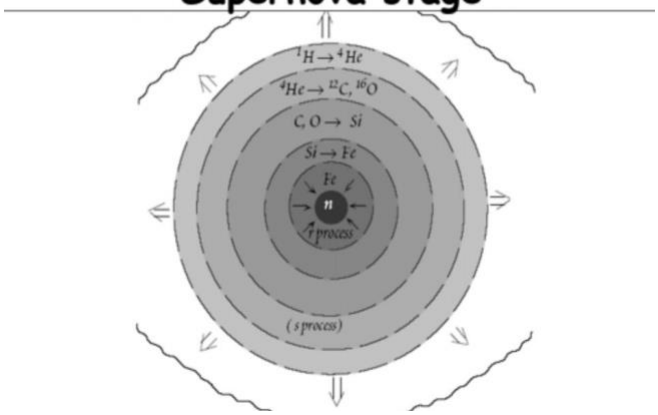
Figure 2.3

After Brownlow, 1996



process	fuel	products	temperature (K)
H-burning	H	He	6E7
He-burning	He	C, O	2E8
C-burning	C	O, Ne, Na, Mg	8E8
Ne-burning	Ne	O, Mg	15E8
O-burning	O	Mg to S	2E9
Si-burning	Mg to S	elements near Fe	3E9

Schematic diagram of stellar structure at the onset of Supernova stage



يبقى النجم في حالة التتابع الرئيسي طالما بقي يدمج الهيدروجين ويتحول الى عملاق احمر عندما ينفذ الهيدروجين ويبدأ بدمج الهيليوم وعندما يصل الى مرحلة تكوين الحديد سينهار لانه ستقل طاقة الطرد المركزي الناتجة عن الاندماج النووي وسينفجر على هيئة مستعر اعظم

PROBLEMS

- How do we know that the Sun is at least a "second generation" star? **Our sun contains H, He, & some heavy elements (e.g. C, O, N) which formed after a supernova explosion of a 1st gen. Star & react as catalysts to speed up the fusion of H**
- Elements with even Z are more abundant than their neighbors with odd atomic numbers, Why? **Elements with even Z are more stable than those with odd Z (Rate of fusion of heavy nucleus with even Z is less than another nucleus)**
- Which 2 elements (besides H & He) exhibit prominent +ve anomalies with respect to their abundance in the solar system? & Explain why these elements have unusually high abundances
  - **Fe: one of the most stable nuclei (has high binding E) & can't be further diffused in a stars**
  - **Pb: formed by decay of unstable radioactive U & during supernova stage (has 2 sources)**
- Why do successive steps in the alpha addition process, which forms nuclei from ^{12}C through ^{56}Fe, require greater T-P? **Alpha are +ve particle, & the +ve charge increases from ^{12}C to 56Fe, so higher T-P are needed to overcome the repulsion forces**
- What element is formed during the main sequence stage of stellar evolution? **Helium (He) only**
- List the following elements in the order you would expect to find them in a massive second-generation star from the core to the outside: He, Si, H, O, & Fe
  - **Fe, Si, O, He, H (relative to decreases T-P from the core to the outside of the star)**
- Check for the abundance of Ar in table 2.1 in textbook & see whether it is greater than expected. If so, suggested an explanation for that! **1.04×10^5 atom/10^6Si, enhanced by the decay of the long lived radioactive isotopes (K), & Ar is formed also during red giant stages in a stars, the 3rd reason that Ar is noble gass so very stable against decay**
- How has the abundance of H in the universe changed since the Big Bang ? **Produced after Big-Bang & then decreases in the formation of He by nuclear fusion in the main sequence stars (decreases with time)**
- Why do technetium (Tc) & promethium (Pm) lack stable isotopes? **Because of their half-life is very short (seconds to years), unstable in most known conditions, & decay rapidly by η-capture**
- List all other elements lack stable isotopes **The elements with Z > 83 (Pu, Cm, Na, Pa, Am, Ra, Bk, Cf, Po, Ac, Es, Fm, Md, Rn, Db)**
- How did lithium (Li), beryllium (Be), & boron (B) form? **When you smash a high-energy particle into a massive nucleus, the large nucleus splits apart into a variety of component particles. This process (spallation) explain how Li, Be, & B form**
- Any of the following elements formed in the stars? (Ar, Pb, U, Ti)? **Ar (other formed during supernova)**

Chapter Two
The Solar System

جميع كواكب المجموعة الشمسية تكونوا على نفس المستوى ما يدل على ان لهم نفس المصدر، وجميعها تدور بنفس الاتجاه حول الشمس، وحول نفسها (باستثناء الزهرة)، والكواكب القريبة عن الشمس صخرية والبعيدة غازية

- **The Sun formed from** a cloud of dust & gas, as with all other stars of the MilkyWay & in the universe
  - In the case of the Sun a very small fraction of the cloud accreted to form a set of 9 planets
  - Diffuse mass of gas & dust (nebula) 6Ga from explosions of ancestral stars (Supernovae)
  - elements formed in these stars were added to H & He (originated from Big Bang)
- **why all planets rotating in the same direction?** The nebula was rotating in the same sense of the Milky way (this explain)
- **why all planets on same level?** The nebula acted upon by gravitational, magnetic, & electrical forces led to Contraction of the rotating desk

H, He: ~99% of all atoms	
of the remaining ~1 %...	
oxygen (O)	55%
carbon (C)	23
nitrogen (N)	7
neon (Ne)	8
magnesium (Mg)	2.5
silicon (Si)	2.3
iron (Fe)	2.1
sulfur (S)	1.2
aluminum (Al)	0.2
calcium (Ca)	0.14
sodium (Na)	0.14
nickel (Ni)	0.11

Chemistry of a solar system

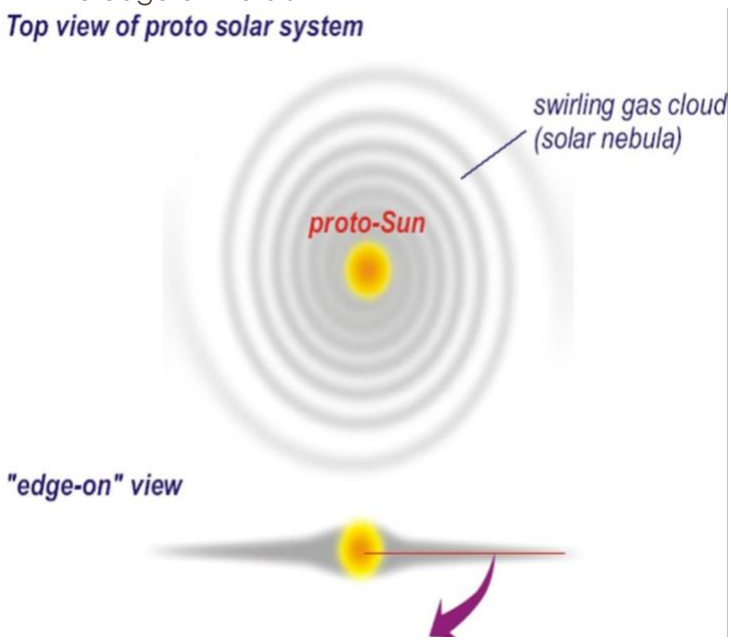
volatile

Gases of from gaseous compound

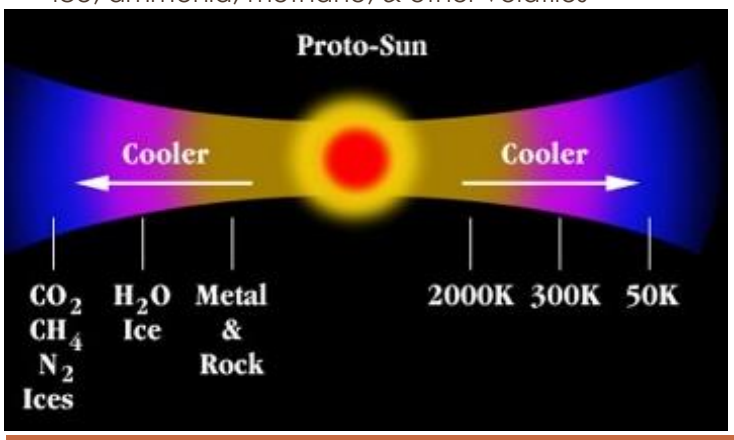
refractory **Tend to form solid at any T**

volatile under some conditions (such as high T)

- **T-P gradients increase in the rate of rotation**: Certain solid particles could not survive T in the center of the nebula & evaporated, only the most refractory particles like Ni-Fe alloys, Al_2O_3, CaO survived, & In the outer part larger number of particles remained in the solid state
- **Why the planets closer to the sun are terrestrial & those further from the sun are Jovian planets?** Increased rate of rotation results in the formation of a protosun in the central disk
- **Why the Jovian planets consist of gas compound such as CH_3 & NH_3 in a solid state?** duo to low T
- The T increased to 2000K at the center to about 40K at approximately 7.5 GKm. form the protosun
- The P ranged from < 0.1 atm to about 10^{-7} atm near the edge of the disk



- Compounds with low vapor P formed dust particles & persisted throughout the nebula & those with high vapor P could exist in the outer cooler regions
- The condensates accreted to form larger bodies due to adhesion caused by electrostatic & magnetic forces (planetesimals 10 m - >1000 km)
- Those close to protosun consisted of refractory minerals, farther away Fe-Mg silicates, farther out ice, ammonia, methane, & other volatiles



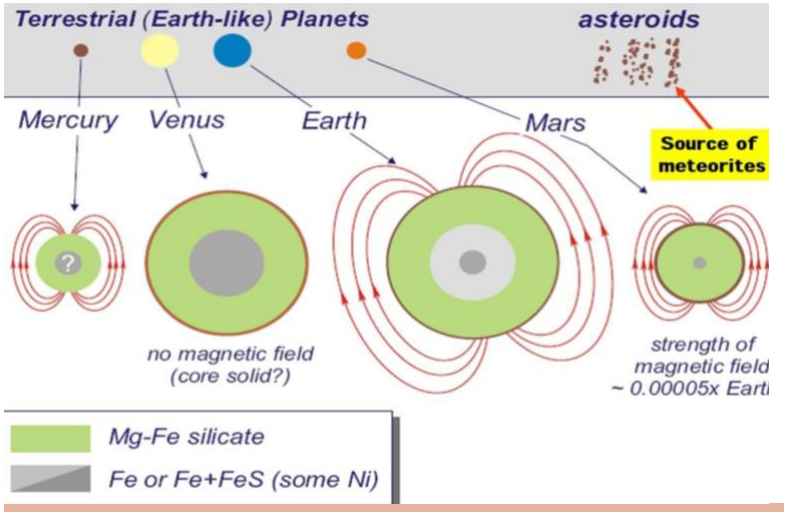
T	Conditions & Reactions
1600	Refractory oxides (CaO, Al_2O_3, TiO_2), & rare e
1300	Metallic Fe, Ni
1200	$MgSiO_3$

1200 - 500	Fe react with O to form $(Fe,Mg)_2SiO_4$
1000	Alkali metals (alminosilicate): $Na + Al_2O_3 \rightarrow$ Alkali-feldspar
675	$H_2S + Fe \rightarrow FeS + 2H^+$
550 - 425	H_2O + Silicates → Hydrous silicates
170	H_2O condenses to water ice
150	$NH_{3(g)} + H_2O_{(s)} \rightarrow NH_3.H_2O_{(s)}$
125	$CH_{4(g)} + H_2O_{(s)} \rightarrow CH_4.7H_2O_{(s)}$

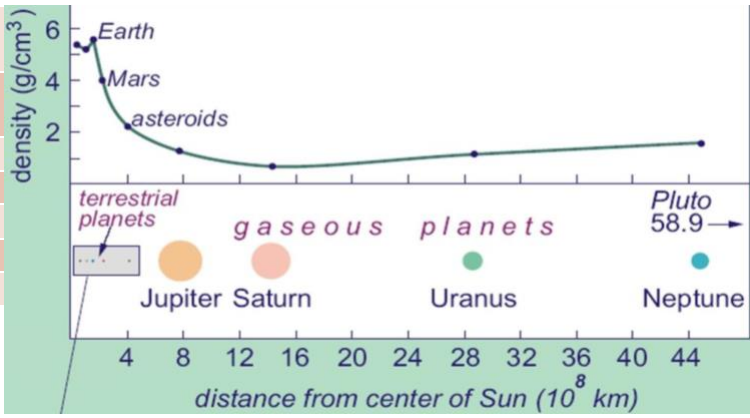
- The sun needed 100,000 to reach T for H burning

Superluminous phase (مرحلة اضاءة عالية جدا)	Initial luminosity was 2-3times greater than main sequence stars, Energy was inherited from the initial contraction, & lasted for about 10 Ma
T-Taure stage	25% of sun mass exploded as solar wind of proton/electron plasma هذه الرياح ازاحت الغلاف الجوي القديم للكواكب القريبة من الشمس
Main sequence	After T-Taure stage the sun entered the main sequence, In the inner part of disk planetesmals accreted to form the **terrestrial planets** & the **asteriods** & Instabilities in the outer part of the disk gave rise to the **Jovian planets**

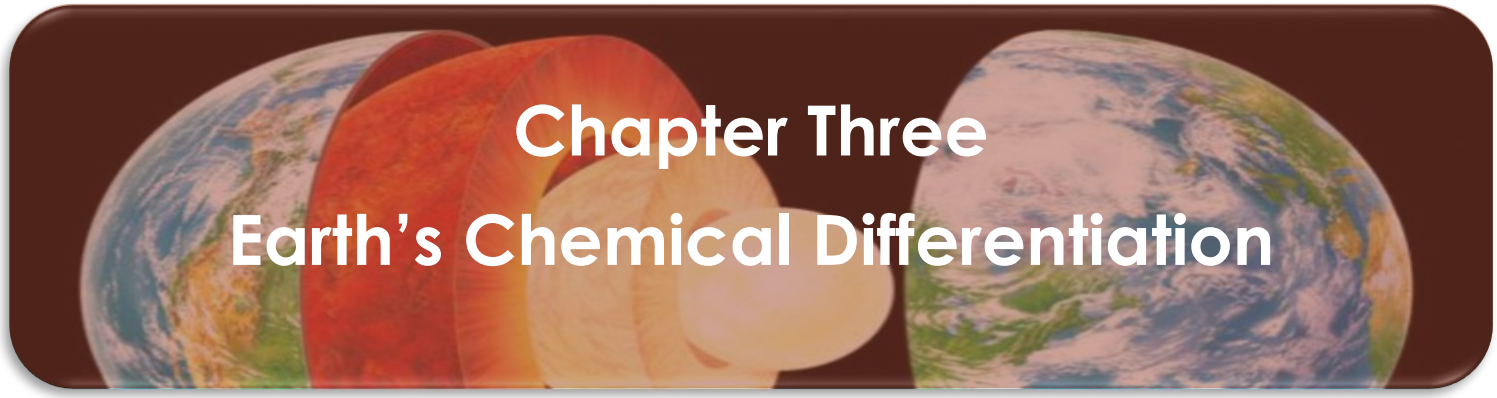
- **Terrestrial planets**: Mercury, Venus, Earth, & Mars
- **Asteriods**: parent material of the meteorites
- **Jovian planets**: Jupiter, Saturn, Uranus, Neptune
- The origin & chemical composition of Pluto aren't known, distance is not consistent with **Titius-Bode**
- **Titius-Bode law**: governs distances of the planets to sun expressed as AU, [(0,3,6,12,24)+4]/10 =(0.4,0.7,1,1.6,2.8) resulting numbers match well with the distances of the planets to the sun with some discrepancies one of which is that of Pluto



The magnetic field is caused by a liquid core



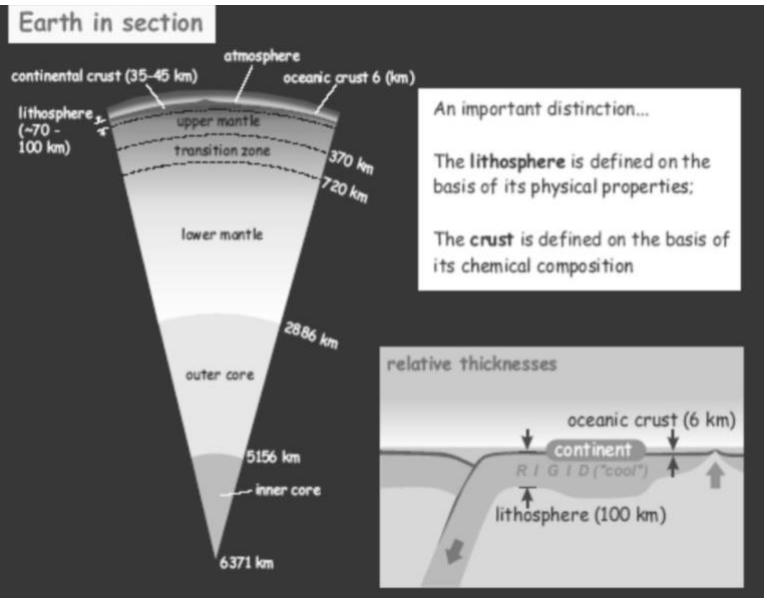
- **The total mass of the solar system** is about 2.052×10^{33}g, 99.87% of which in the sun & 0.13% for the 9 planets (71% in Jupiter, 0.0006% of the total mass in terrestrial planets & moon)
- **Earth**: covered by 71% water & have developed life
- The earth-like planets were first molten because of heat generated by capturing of hot planetismals & radioactive heating
- The last phase of their formation was the capturing of planetismals composed of volatiles called cometismals, & These deposited solids of water, methane & ammonia on the surface of the planets
- The water & other volatiles evaporated to form the atmosphere from which water ultimately condensed as the surface of the Earth cooled
- Mercury & the moon do not have atmosphere since they were too small to retain the gases
- Mars & the moon cooled sufficiently shortly after their formation & became geologically inactive while Earth & Venus being the largest are active
- Mars, being intermediate in size has volcanic activity not too distant in the geologic past
- Venus has a CO_2 atm so it became hot & dry while the earth cooled rapidly allowing oceans to form > 4Ga by condensation of water vapor in atmosphere
- The formation of hydrosphere (oceans) permitted geological processes to operate & the lead to the development of life
- Terrestrial planet hadn't He, H forming atm, since both elements had been expelled from the inner regions during the T-Taure stage of the sun
- Earth accretion models:
  1. **Homogeneous model:** initially assembled from silicate & Fe (uniformly mixed), & heat-up cause catastrophic differentiation by core infall
  2. **Heterogenouse model:** Earth assembled in step-wise fashion (core, then silicate mantle)



Chapter Three
Earth's Chemical Differentiation

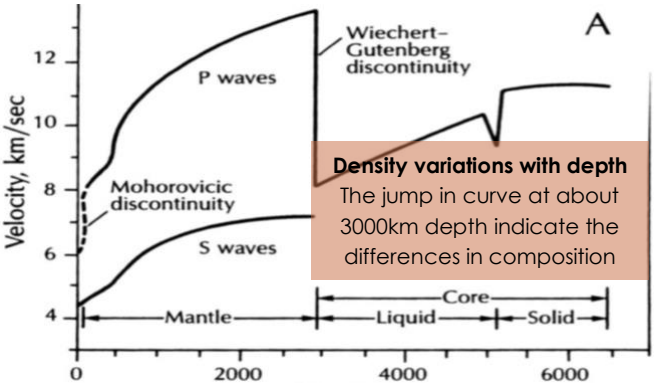
EARTH'S SPHERES & DIFFERENTIATION

- **Differentiation**: separation of the Earth into shells of different compositions
- The Earth is a highly differentiated planet (Evidence of that is the existence of layers)
- Differentiation caused by active geological processes which leading to further diversity in its shells & their constituent rocks.

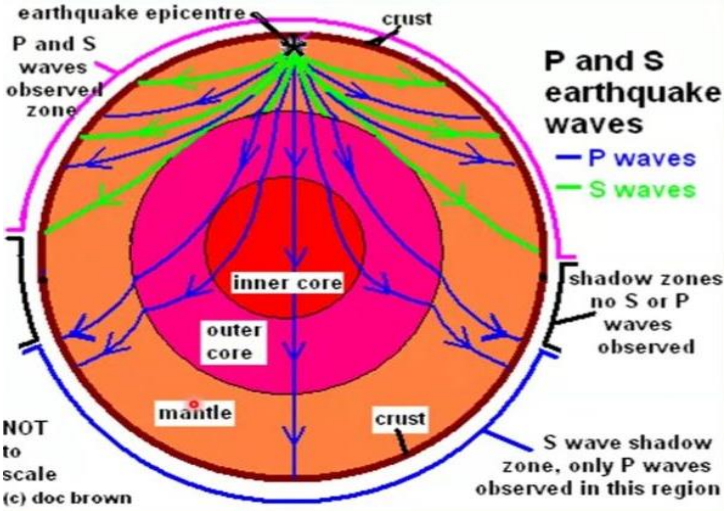


- Depending on chemical or mineralogical composition: Crust, Mantel, & Core
- Depending on physical properties

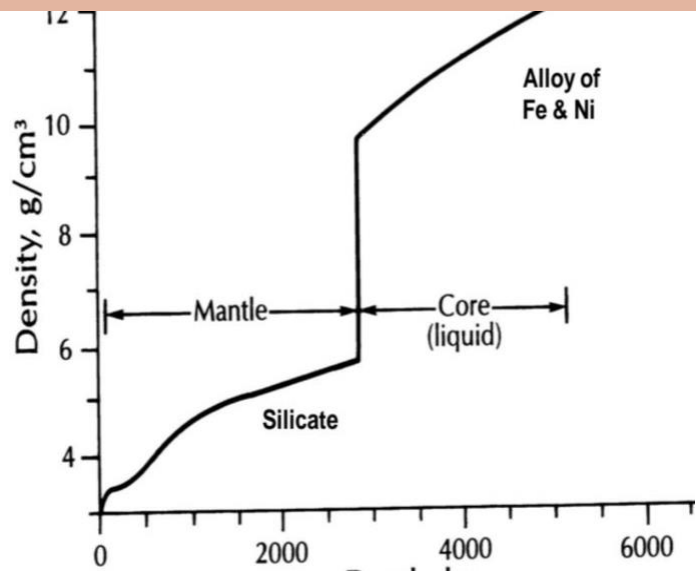
Lithosphere	Crust & upper mantle, solid
Moho boundary	between crust & mantle, 100km
Asthenosphere	consist of fluids
Gutenberg	between mantel & core, 2890km
Outer core	Liquid
Inner core	Solid



Density variations with depth
The jump in curve at about 3000km depth indicate the differences in composition



Seismic V variations with depth: Region with high anomalies (where S-wave disappeared & P-wave V dropped) indicate the boundaries between different layers & zones



	Thickness [km]	Volume [10^{27}cm³]	Density [g/cm³]	Mass [10^{27}g]	Mass%
Earth	6371	1.083	5.52	5.976	100%
Core	3471	0.175	10.7	1.876	31.5%
Mantle	2883	0.899	4.5	4.075	68.1%
Crust	40	0.00824	2.8	0.0236	0.4%
Hydrosphere	3.8	0.00137	1.03	0.0014	0.024%
Atmosphere	—	—	—	$5x10^{-6}$	$9 x10^{-5}$

Most of the earth's mass is in mantle
The denser layer is core, & the Avg. ρ of surface is 2.8g/cm³
The thickest layer in core & thinner is crust

CHEMICAL COMPOSITION OF THE MANTLE

	Sample 1[a]	Sample 2[b]	Sample 3[c]
SiO_2	45.2	48.1	45.0
MgO	37.5	31.1	39.0
FeO	8.0	12.7	8.0
Al_2O_3	3.5	3.1	3.5
CaO	3.1	2.3	3.25
Na_2O	0.57	1.1	0.28
Cr_2O_3	0.43	0.55	0.41
MnO	0.14	0.42	0.11
P_2O_5	0.06	0.34	—
K_2O	0.13	0.12	0.04
TiO_2	0.17	0.12	0.09
NiO	—	—	0.25
Sum	98.8	99.95	99.93

[a]Pyrolite (Ringwood, 1966).
[b]Mantle plus crust based on meteorites (Mason, 1966).
[c]Undepleted mantle based on lherzolites (Hutchison, 1974).

Pyrolite (hypothetical) = 3peridotite +1basalt

Xenoliths brought to the mantle indicate: pyroxene, olivine, Spinel, amphibole, garnet

Meteorites: less differentiated

Ultramafic rocks

Found in upper mantle

CHEMICAL COMPOSITION OF THE CONTINENTAL CRUST

- **Continental crust include** atmosphere, hydrosphere, biosphere, & part of the lithosphere & consists of 2 principal parts: oceanic & continental

Crust	Consist of
Oceanic	Basalt with a thin layer of sediments
Continental	95% igneous & metamorphic rocks 5% sedimentary cover

	Poldervaart				Ronov and Yaroshevsky
	1 Continental shields[a]	2 Young folded belts[b]	3 Suboceanic regions[c]	4 Deep oceanic[d]	5 Oceanic crust
SiO_2	59.8	58.4	49.4	46.6	49.4
TiO_2	1.2	1.1	1.9	2.9	1.4
Al_2O_3	15.5	15.6	15.1	15.0	15.4
Fe_2O_3	2.1	2.8	3.4	3.8	2.7
FeO	5.1	4.8	6.4	8.0	7.6
MnO	0.1	0.2	0.2	0.2	0.3
MgO	4.1	4.3	6.2	7.8	7.6
CaO	6.4	7.2	13.2	11.9	12.5
Na_2O	3.1	3.1	2.5	2.5	2.6
K_2O	2.4	2.2	1.3	1.0	0.3
P_2O_5	0.2	0.3	0.3	0.3	0.2

Chemical composition of 4 major structural unit of lithic crust in Wt%
Shields: all rock from Precambrian (older then 550Ma)
Mobil belts: rocks that formed after Cambrian (younger 550Ma)

- Different estimates for the composition of the crust:
  1. averaging large number of chemical analyses
  2. combining chemical analyses of different rock types weighted by their abundances
  3. analyzing sediments derived from continents
  4. combining compositions of acidic & mafic rocks
  5. modeling (mathmatical)

	1[a]	2[b]	3[c]	4[d]	5[e]	6[f]	7[g]	8[h]
SiO_2	59.12	59.07	59.19	60.06	59.4	59.3	57.3	68.4
TiO_2	1.05	1.03	0.79	0.90	1.2	0.7	0.9	0.4
Al_2O_3	15.34	15.22	15.82	15.52	15.6	15.0	15.9	14.8
Fe_2O_3	3.08	3.10	3.41	3.55	2.3	2.4	—	1.3
FeO	3.80	3.71	3.58	4.06	5.0	5.6	9.1	3.2
MnO	0.12	0.11	0.11	0.21	0.1	0.1	—	—
MgO	3.49	3.45	3.30	3.56	4.2	4.9	5.3	1.7
CaO	5.08	5.10	3.07	5.62	6.6	7.2	7.4	3.4
Na_2O	3.84	3.71	2.05	3.28	3.1	2.5	3.1	3.1
K_2O	3.13	3.11	3.93	2.88	2.3	2.1	1.1	3.6
P_2O_5	0.30	0.30	0.22	0.36	0.2	0.2	—	0.1
CO_2	—	0.35	0.54	—	—	—	—	—
H_2O	1.15	1.30	3.02	—	—	—	—	—

Taylor & McLennan 1985

Average composition of continental crust in Wt%
1st Clarke & Washington: analysis of igneous from all continents
2nd Clarke & Washington: 95% ig + 4% shale + 0.75 Ss + 0.25% Ls
3rd Goldschmidt: based on 77 analyses of glacial clay
4th Daly: based on 1:1 mixture of average granite and basalt
5th Polderwart: average folded belts & continental shield regions

- The composition of the continental crust is completely different from that of the solar nebula or the stony meteorites

Elemental Abundances in Earth's Crust		
Elements	**Whole crust**	**Continental crust**
Oxygen (O)	46%	45.5%
Silicon (Si)	28%	26.8%
Aluminum (Al)	8%	8.4%
Iron (Fe)	6%	7.06%
Magnesium(Mg)	4%	3.2%
Calcium (Ca)	2.4%	5.3%
Potassium (K)	2.3%	0.9%
Sodium (Na)	2.1%	2.3%
Total	98.8%	99.46
Other element present in traces [expressed in ppm, ppb]		

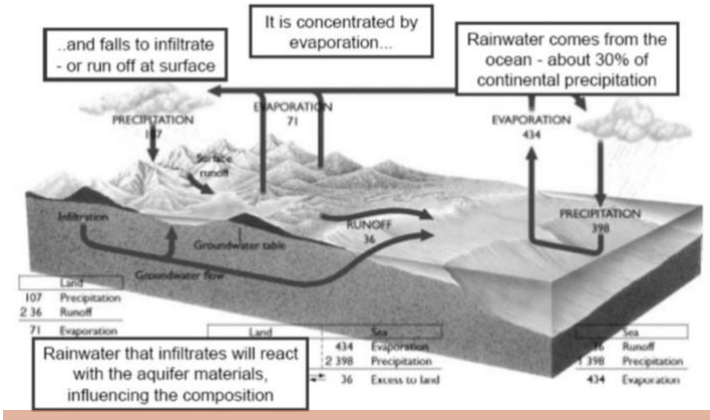
DIFFERENTIATION OF IGNEOUS & SEDIMENTARY ROCKS

- **The composition of the igneous rocks is highly variable due to** geochemical differentiation that takes place during their formation
- **The differentiation starts from** the time of igneous rocks formation by partial melting of upper mantle or lower crustal rocks
- **The composition of the melt depends on** the composition of the source & extent of the melt which is a function of P-T
- **The composition of the magma may be modified later on by**: Assimilation of rocks (partially melting of magma chamber), Mixing with other magmas, Fractional crystallization, & Liquid immicibility
- **Sedimentary rocks highly diversified like igneous by**: Weathering, Transport, Deposition, & Lithification

Element, Z	Ultramafic[a]	Basalt[a]	High-Ca granites[b]	Low-Ca granites[b]	Shale[b]	Sandstone[b]	Carbonate rocks[b]	Deep-sea clay[b]
3 Li	0.5	16	24	40	66	15	5	57
4 Be	0.2	0.7	2	3	3	—	—	2.6
5 B	2	5	9	10	100	35	20	230
9 F	100	385	520	850	740	270	330	1300
11 Na (%)	0.49	1.87	2.84	2.58	0.96	0.33	0.04	4
12 Mg (%)	23.2	4.55	0.94	0.16	1.50	0.70	4.70	2.10
13 Al (%)	1.2	8.28	8.20	7.20	8	2.50	0.42	8.40
14 Si (%)	19.8	23.5	31.40	34.70	7.30[c]	36.80	2.40	25
15 P	195	1130	920	600	700	170	400	1500
16 S	200	300	300	300	2400	240	1200	1300
17 Cl	45	55	130	200	180	10	150	21000
19 K (%)	0.017	0.83	2.52	4.20	2.66	1.07	0.27	2.50
20 Ca (%)	1.6	7.2	2.53	0.51	2.21	3.91	30.23	2.90
21 Sc	10	27	14	7	13	1	1	19
22 Ti	300	11400	3400	1200	4600	1500	400	4600
23 V	40	225	88	44	130	20	20	120

A partial chemical composition of some igneous & sedimentary rocks (in ppm which equal to mg/L)

Hydrosphere



Differentiation of the hydrosphere

Evaporation (by heat from the sun) → Condensation → Precipitation

Reservoir	Volume $10^6 km^3$	Vol%
Ocean	1370	97.25%
Ice sheet (glaciers)	29	2.05%
Groundwater	**9.5**	**0.68%**
Lakes	**0.125**	**0.01%**
Soil moisture	0.065	0.005%
Atmosphere	0.013	0.001%
Rivers	**0.0017**	**0.0001%**
Biosphere	0.0006	0.00004%
Total	1408.7	100%

Inventory of water in the hydrosphere

When water come in contact with rocks different types of chemical weatherin or water rock interactions

SUSCEPTIBILITY OF MINERALS TO WEATHERING

- The susceptibility of minerals to weathering is different (opposite to Bowen's reaction series), so the elements in the rocks don't enter into aqueous medium in the same proportions as in rocks
- The chemical elements become subjected to a variety of processes when they enter hydrosphere:
  1. Some selectively absorbed on charged surfaces of clay minerals or oxides & hydroxides
  2. Others enter the biosphere as nutrients & associated with organism & biogenic carbon
  3. Noble gases are released into the atmosphere

Element	Classification[a]	Stream water	Seawater	Seawater enrichment	MORT[b]
Li	I	3×10^{-3}	1.7×10^{-1}	56.7	2.5×10^{6}
Be	IV	1×10^{-5}	2×10^{-7}	0.02	6.3×10^{1}
B	I	1×10^{-2}	4.5	450	1.6×10^{7}
F	I	1×10^{-3}	1.3	1300	7.9×10^{5}
Na	I	6.3	1.08×10^{4}	1714	2.0×10^{8}
Mg	I	4.1	1.29×10^{3}	315	5.0×10^{7}
Al	IV	5×10^{-2}	8×10^{-4}	0.016	7.0
Si	II	6.5	2.8	0.43	7.9×10^{3}
P	II	2×10^{-2}	7.1×10^{-2}	3.6	4.0×10^{4}
S	I	3.7	9.0×10^{2}	243	5.0×10^{8}
Cl	I	7.8	1.95×10^{4}	2500	6.3×10^{8}
K	I	2.3	3.99×10^{2}	173	1.3×10^{7}
Ca	I	15	4.13×10^{2}	27.5	1.3×10^{6}
Se	III	6×10^{-3}	1.3×10^{-4}	2.2	$6.3 \times 10^{-}$
Br	I	2×10^{-2}	6.7×10^{1}	3350	7.9×10^{8}
Rb	I	1×10^{-3}	1.2×10^{-1}	120	7.9×10^{5}
Sr	I	7×10^{-2}	7.6	109	5.0×10^{6}
Y	III	4×10^{-5}	7×10^{-6}	0.18	1.3×10^{2}
Zr	IV	—	3×10^{-5}	—	1.6×10^{2}
Nb	IV	—	$<5 \times 10^{-6}$	—	$<2.5 \times 10^{2}$

Biological activity

Average composition of water in stream & ocean (µg/g)

I = conservative & constant concentration throughout the ocean

II= non-conservative, concentration changes vertically & horizontally

III = non-conservative but the concentration changes irregularly

IV = unclassified but probably nonconservative

MORT = Main Oceanic Residence Time [in years] (فترة المكوث)

بعض العناصر لا تمكث كثيرا لانه يتم استهلاكها مثل Si, P، وبعضها (heavy elements such as U) يحدث لها absorption بجزيئات ال clay والتي تترسب على قاع المحيط لذا فتركيزها قليل

$t = A_x/(dx/dt)$ = Σamount of element/Avg. annual input of that element

Seawater Enrichment = $[X]_{seawater}/[X]_{Streamwater}$

من المفترض ان تركيز بعض العناصر (Si, P) يكون اكبر بالمحيطات من تركيزه في الانهار لان النهر يصب في المحيط ولكن الواقع تركيزه اقل بسبب استهلاكه من قبل الكائنات الحية في المحيط

يزداد تركيز الصوديوم بالمحيطات (يزيد الملوحة) لان املاحه ذائبيتها عالية لذا فيبقى بشكله الايوني

- The chemical composition of the water affected by rocks composition & geochemical environment
- Geochemical environment determined by :climate, topography, & vegetation

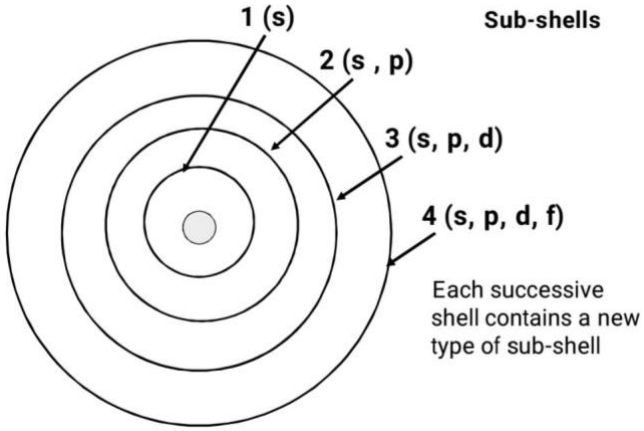
Average enrichment factors	
Alkali metals	416 (14.5-1,714)
Alkaline earths (excepts Be & Ba)	151 (27.5-315)
Halogens	1,790 (8-3,350)

Percentages of chemical elements in the earth		
Element	Wt%	
Iron Fe	36.0%	**Whole Earth** The iron is most common element in the earth, then Oxygen, & then Silicon
Oxygen O	28.7%	
Silicon Si	14.8%	
Magnesium Mg	13.6%	
Nickel Ni	02.0%	
Calcium Ca	01.7%	
Sulfur S	01.7%	
Aluminum Al	01.3%	
Chromium Cr	00.5%	
Phosphorus P	00.2%	
Cobalt Co	00.1%	
Oxygen O	46.6%	**Earth's Crust**
Silicon Si	27.7%	
Aluminum Al	08.1%	
Iron Fe	05.0%	
Calcium Ca	03.6%	
Sodium Na	02.8%	
Potassium K	02.6%	
Magnesium Mg	02.1	

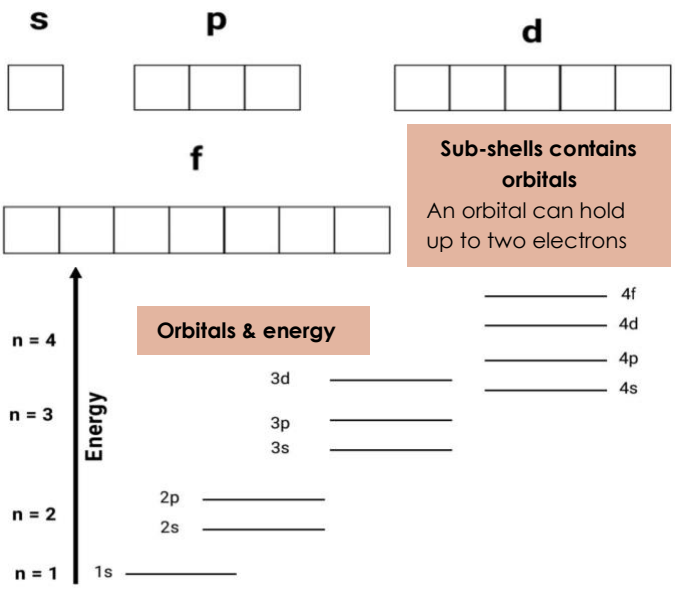
Chapter Four
Electronic Structure, Periodic Table, & Chemical Bonding

ELECTRONIC STRUCTURE OF ATOMS

- The electrons are concentrated at various specific distances from the nucleus in the form of orbitals that can be thought of as volumes of space in which the electrons are most likely to occur

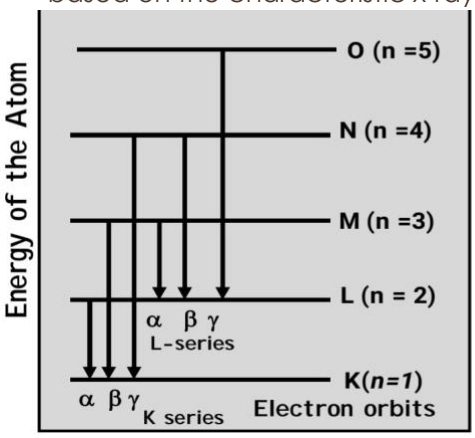


Shells (principal quantum number)
Electrons in specific orbital has a specific energy state, max number of shells around nucleus is 7 (K, L, M, N, O, P, & Q) & every one has maximum capacity of electrons (K=2,L=8…)
Sub-shells: (s), (s, p), (s, p, d), & (s, p, d, f)



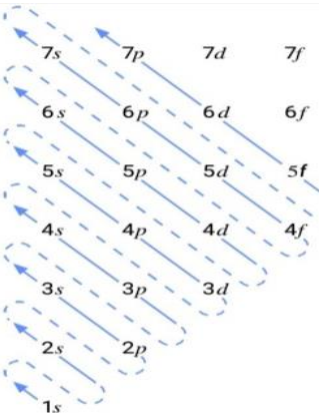
Electronic transition	Characteristic X-ray
L to K	K-α (alpha)
M to K	K-β (beta)
N to K	K-γ (gamma)
O to K	K-Δ (delta)

- The diffraction (XRD) is based on the diffraction of x-rays by the crystal lattice, X-ray fluorescence is based on the characteristic x-rays by the elements

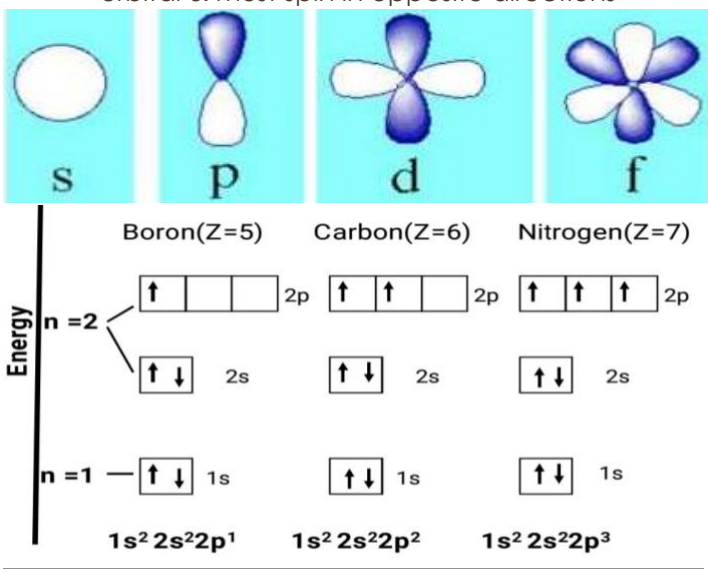


Schematic energy level diagram of atoms based on Bohr's model

- **Schrödinger Model:** equation for both the wave & particle properties of the electron, gives the probability of finding electron in a particular orbital by using electron density & a wave function equation



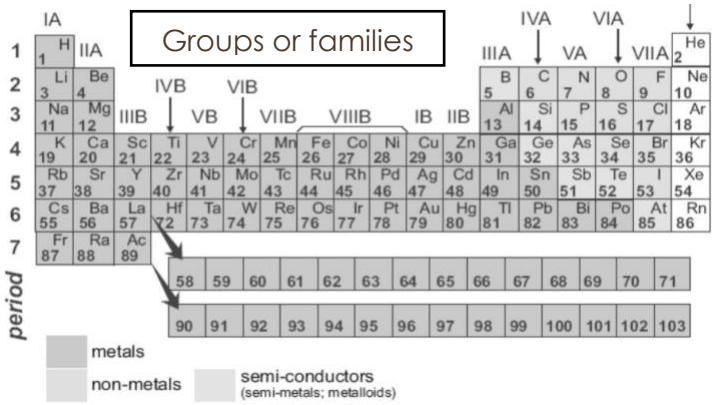
- **The Aufbau Principle (building up principle):** electrons are put into orbitals in order of increasing subshell energy
  - a maximum of 2 electrons can occupy the same orbital & must spin in opposite directions



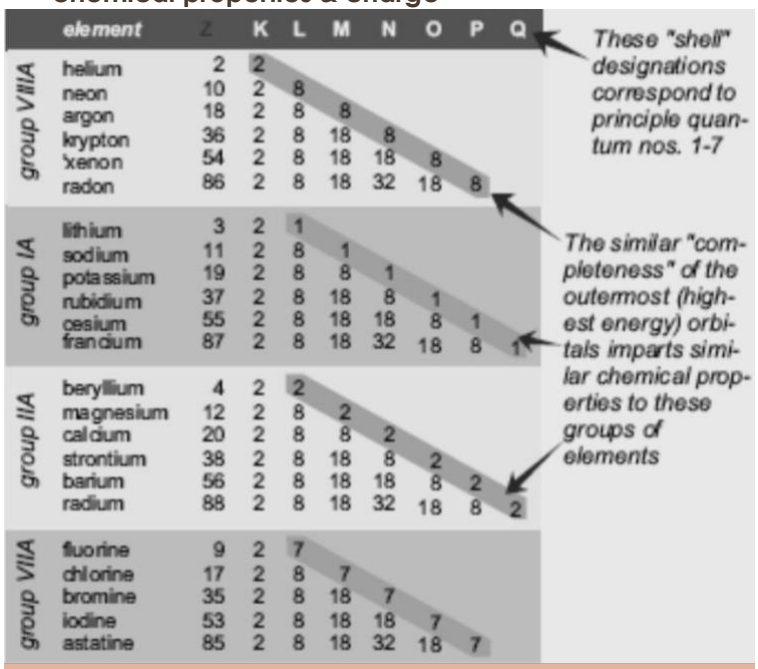
Examples: Z(C =6, Si =14, & Ge=32)

- C = $1s^2 2s^2 2p^2$
- Si = $1s^2 2s^2 2p^6 3s^2 3p^2$ = $[Ne]3s^2 3p^2$
- Ge = $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^2$ = $[Ar]4s^2 3d^{10} 4p^2$

THE PERIODIC TABLE



- **Period** Horizontal arrangement have same physical properties, **Groups** vertical arrangement have same chemical properties & mostly same charge
- **The element in the periodic table can be divided into 2 group passed on physical properties**: Matals & Non-Metals
- **Every groups in a periodic table have same chemical properties & charge**



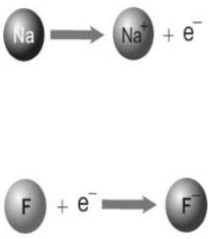
الذي يحدد الخصائص الكيميائية هو التوزيع الالكتروني
مثلا عناصر المجموعة الثامنة VIIIA لديها نفس العدد من الاكترونات في المدار الاخير (8) والمجموعة الاولى IA لديهم الكترون واحد في المدار الاخير وهكذا
وبالتالي المجموعات A كلها لها عدد الكترونات = رقم المجموعة في المدار الاخير
اما ال period فتشترك كلها في نفس عدد ال orbitals ويساوي عدد الالكترونات

Metals (bellow) & Non-Metals (above)

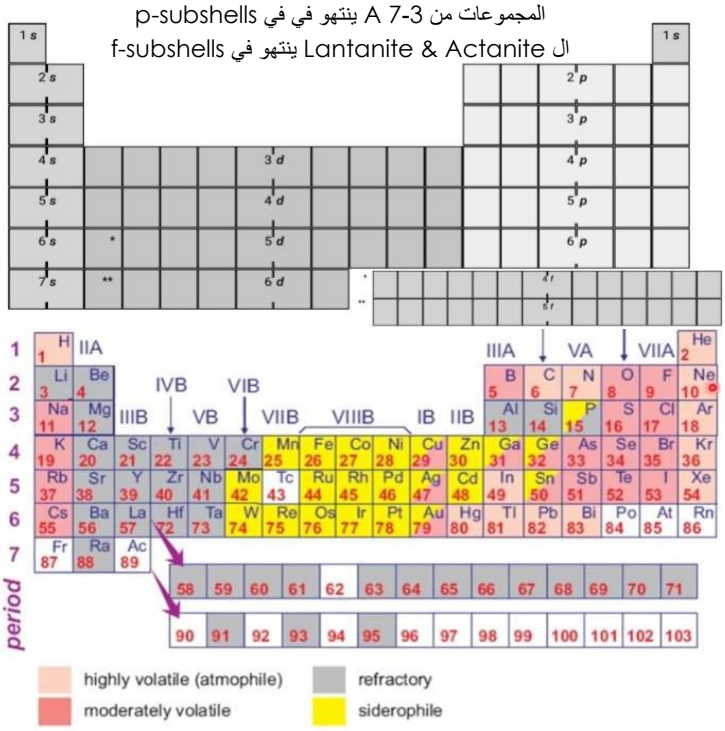
Non metals properties increases from left to right in the periodic table

Metals: tend to loss e^- to form cations

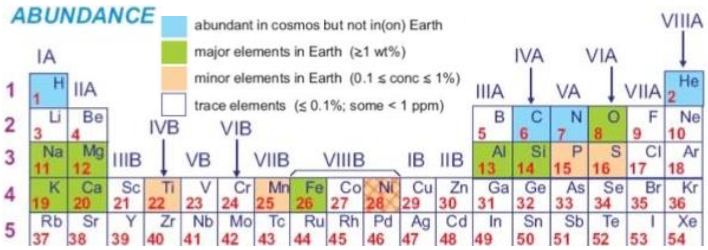
Non-Metals: tend to gain e^- to form anions



المجموعات 1,2 تنتهيان ب s-subshells لذا تسمى S block
ال transition metals ينتهو في d-subshells
المجموعات من 3-7 A ينتهو في في p-subshells
ال Lantanite & Actanite ينتهو في f-subshells

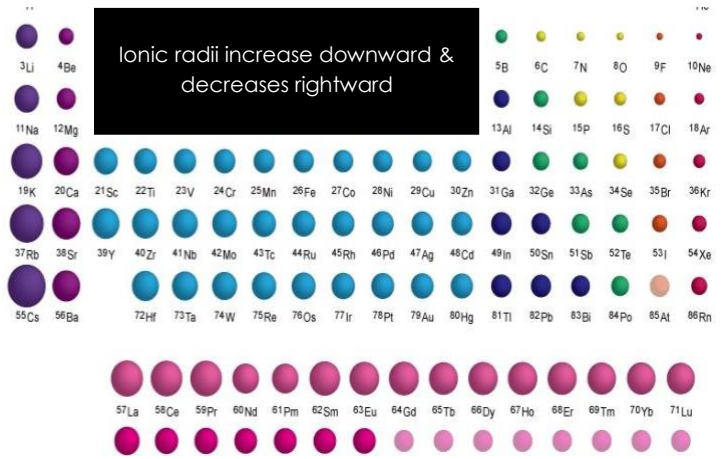


- **High volatile:** always in gaseous state (H, C, N, Nobel gases..)
- **Moderately volatile:** It tends to be in the gaseous state under moderately to high T (Na, K, Rb, Cs, O, F,…)
- **Refractory:** always in solid state (have high Boiling point), alkali earthy elements, most transition elements, Al, & Si…
- **Siderophile:** mostly attached to sulfur & have properties same as iron (Mn, Mo, Pd…)
- **Radioactive elements:** unstable isotopes (such as U)



- Anions have more ionic radii than cations because they grains electrons

مثلا F يحتوي 7e بالمدار الاخير اذا اكتسب الكترون يصبح 8e فتزداد قوى التنافر بين الاكترونات في المدار الاخير فيزداد حجم الايون



ISOTOPES

- **Isotopes**: atoms of the same element (Z) with different mass number (atomic mass A), have same number of protons but different number of neutrons
- **Atomic number Z:** is a number of protons
- **Mass number or atomic mass A:** is a number of protons + number of neutrons

- Isotopes can be subdivided into 2 groups:
  1. **Stable isotopes:** Don't decay (^{16}O, ^{12}C..)
  2. **Unstable isotopes:** Decayed with time to reach equilibrium state such as (U → Pb)
- Most elements have ≥ 2 stable isotopes
- Some have long-lived radioactive isotopes
- large group of short-lived radio isotopes does occurs in nature
- Isotopes of elements are found in nature with different abundances

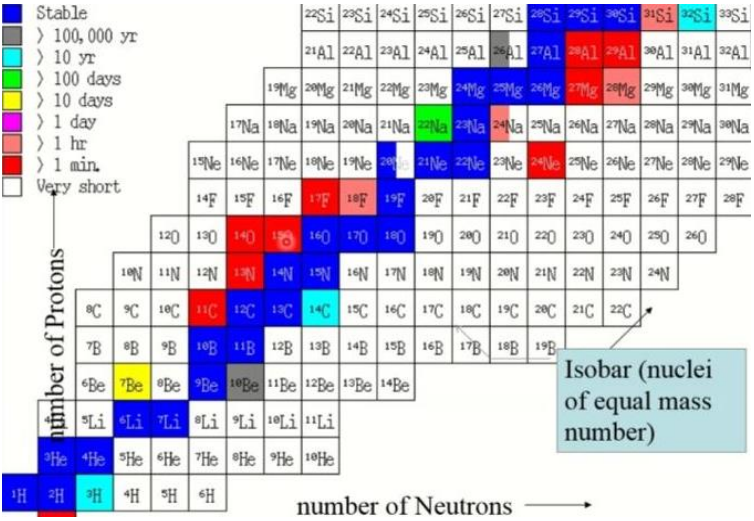


Chart of the Nuclides

- **Hhalf-life:** time required to decay 50% an isotopes
- **Atomic weight:** is a sum of a masses of its naturally occurring isotopes weighted in their abundance

For example Si has 3 naturally occurring isotopes & the atomic weight is found by multiplying the masses of isotopes by their abundance expressed as decimal fraction & adding the result product:

Isotopes	Abundance	Mass (amu)	A*m (amu)
$^{28}_{14}Si$	92.23%	27.976927	25.80312
$^{29}_{14}Si$	4.67%	28.976495	1.35320
$^{30}_{14}Si$	3.10	29.973770	0.92918

Atomic weight (or atomic mass) = sum of A*m = 25.80312 + 1.35320 + 0.92918 = 28.0855 ≈ 28amu

- In the periodic table atomic mass (Atomic weight) calculating in this way for all elements
- 1amu = $^{12}C/12$

SOLUBILITY & NUMBER OF MOLES

- **Mole (mol)**: a number of atoms or molecules (known as Avogadro's number = 6.022045 x 10^{23}atoms)
  1. The gram-atomic weight of an element is equal to its atomic weight in grams
  2. The gram-molecular weight for a compound is the molecular weight in grams
- **Number of mol** = mass/molar mass (n = m/Mw)
- **Gram Formula Weight (GFW)**: weight of 1mol
- **Solubility S** = n/100mL = g/100mL

Example : $2H_2 + O_2 = 2H_2O$

2 mole + 1mole = 2moles

$12.04 \times 10^{23} H_{atoms} + 6.02 \times 10^{23} O_{atoms} = 6.02 \times 10^{23} H_2O_{atoms}$

2g + 1g ≠ 2grams

Example : Barite $BaSO_4$, & Solubility in cold water = 2.22×10^{-4} g/100mL (Ba =137.0, S =32.1, O= 16.0)

1. Calculate GFW in gram (**GFW = Σn*Mw**)
2. Calculate solubility in mol/L (**n=m/Mw**)
3. Calculate # of barite ions in 1L solution (**n*Av**)

Solutions

1. **GFW** = $(n*Mw)_{Ba} + (n*Mw)_S + (n*Mw)_O$ = (1*137) + (1*32.1) + (4*16) = 233.1g/mol
2. **S** = 2.22×10^{-4}mol/23.31L = 9.52×10^{-6} mol/L
3. $BaSO_4 \rightarrow Ba^{2+} + SO_4^{2-}$ ($n_{BaSO_4} = n_{SO_4^{2-}} = n_{Ba^{2+}}$)

   $n_{Ba^{2+}} = 9.52 \times 10^{-6} * 6.02 \times 10^{23} = 5.73 \times 10^{18}$ Ions/L

Example How many moles of Na^+ are present in one liter of an aqueos solution of Na_2SO_4 containing 4.760g of the compound (Mw: Na=23.0, S= 32.1, O=16.0)

Solution

$Na_2SO_4 \rightarrow 2Na^+ + 1SO_4^{-2}$ ($n_{Na_2SO_4} = 2n_{Na^+} = n_{SO_4^{-2}}$)

$Mw_{Na_2SO_4}$ = ΣMw = 142.1g/mol

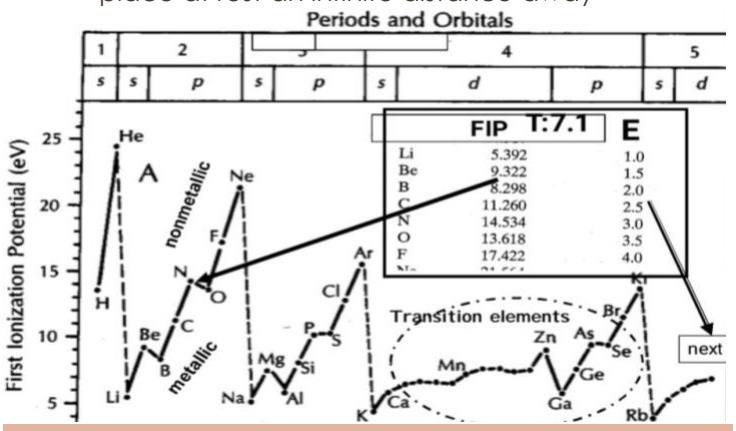
$n_{Na_2SO_4}$ = m/Mw = 4.760/142.1 = 0.0335mol

$n_{Na_2SO_4} = 2n_{Na^+}$ = 2*0.0335mol = 0.0670mol

CHEMICAL BONDS, IONIC RADII, &CRYSTALS

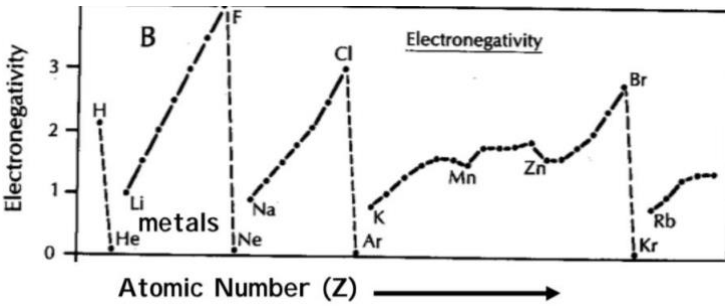
- The physical & chemical properties of the elements vary with increasing Z according to the periodic law
- **elements divided into 2 major groups according to tendency to give or attract electrons:** on the left side of periodic table are electron donors (metals) & on the right are electron acceptors (non-metals)
- **cation**: +ve charged ions, formed by e-donor atoms
- **anions**: -ve charge, formed by e-acceptor atoms
- **Ionic bond:** Formed by electrostatic force between ions of opposite charge (Metals Cation, +ve + Non-Metals Anion, -ve)
  - Most minerals are compounds of cations & anions held together by ionic bond (e.g. Halite)
- **Covalent bond:** sharing of electron among element
  - Formed due to difference in electronegativity χ
  - Formed when 2 elements of similar metallic or nonmetallic character interact
  - electrons shared instead of transferred
- The elements share electrons **unequally** so covalent bonds tend to have ionic character

- The transfer of e- on opposite sides of the periodic table is **never 100**%, so ionic bond have a covalent character (amount is a function of the difference in the tendency of the atoms to attracts electrons)
- **Truly covalent bonds** occur when atoms of same element combine to form molecule (e.g. H_2, O_2, N_2)
- **Parameters to quantify or predict type of bonding**
  1. **First ionization potential energy**: remove one electron from a neutral atom in a vacuum & to place at rest an infinite distance away



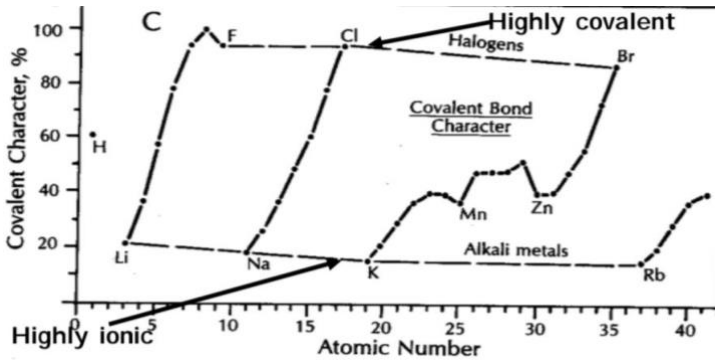
First ionization potential
Metals has higher First Ionization Energy than Non-Metals
So metals loss their electrons faster than Non-Metals

  2. **Electronegativity**: measure of the ability of an atom in a molecule to attract electrons to itself

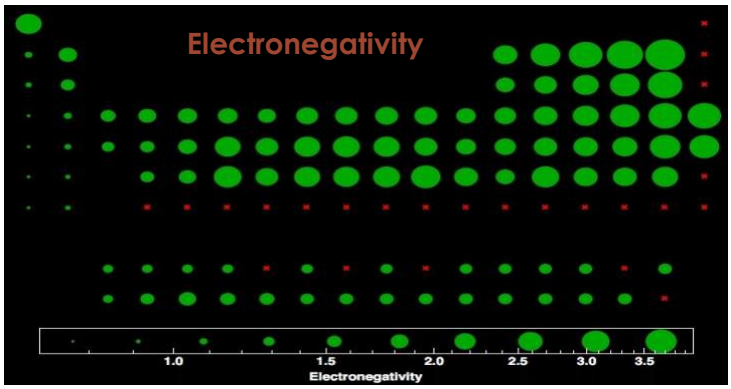


Electronegativity (χ or δ-)
Non-Metals have higher electronegativity then metals (have more affinity to gains electrons)

  3. **Standard electrode potential**: voltage generated when mole of electrons is removed from mole of element "in the standard state"



Covalent character for oxides (FO, ClO..)
Variation of covalent bond character of single bonds with oxygen based on electronegativity differences
For example: Lithium oxide has 20%Covalent + 80%ionic



Percentage of ionic character of single bonds with O			
Δχ	Ionic character %	Δχ	Ionic character %
0.1	00.5%	1.7	51.0%
0.2	01.0%	1.8	55.0%
0.3	02.0%	1.9	59.0%
0.4	04.0%	2.0	63.0%
0.5	06.0%	2.1	67.0%
0.6	09.0%	2.2	70.0%
0.7	12.0%	2.3	74.0%
0.8	15.0%	2.4	76.0%
0.9	19.0%	2.5	79.0%
1.0	22.0%	2.6	82.0%
1.1	26.0%	2.7	84.0%
1.2	30.0%	2.8	86.0%
1.3	34.0%	2.9	88.0%
1.4	39.0%	3.0	89.0%
1.5	43.0%	3.1	91.0%
1.6	47.0%	3.2	92.0%

Examples

$H_2 = \chi H - \chi H = 2.1 - 2.1 = 0 \rightarrow$ 100%covalent
$ZnS = \chi S - \chi Zn = 2.5 - 1.6 = 0.9 \rightarrow$ 19%ionic
$CCl_4 = \chi Cl - \chi C = 3.0 - 2.5 = 0.5 \rightarrow$ 6%ionic
$H_2O = \chi O - \chi H = 3.5 - 2.1 = 1.4 \rightarrow$ 39%ionic
$CaF = \chi F - \chi Ca = 4.0 - 1.0 = 3.0 \rightarrow$ 89%ionic
$KCl = \chi Cl - \chi K = 3.0 - 2.2 = 0.8 \rightarrow$ 15%ionic

- **Importance of bonding:** All physical & chemical properties depend on the character of the bonds
  - **Chemical properties:** Ionic bond have high aqueous solubility (solubility of a compound increases with increasing ionic character)
  - **Physical properties:**
    I. **Isotropic**: Ionic bond tend to be isotropic, & covalent bond tend to be anisotropic
    II. **Resistance to weathering:** minerals with ionic bond are less resistance (such as OI)

Example: calcite dissolved in water as ($CaCO_3 \rightarrow Ca^{2+} + CO_3^{2-}$) & doesn't give rise as ($CaCO_3 \rightarrow Ca^{2+} + C^{4+} + 3O^{2-}$) because C-O are covalent (less aqueous solubility) while the Ca-CO_3 are ionic (high solubility)

- Solubility of ionic bonding crystals in water are related to polarity of water molecules (unequal sharing of electrons due to Δχ between O & H)
  - O attract e- of H & this unequal sharing results in polarity (-ve charge on O & +ve on H) so water attracted to charges on surface of ionic crystal & have no effect on the covalent crystals

- The ions that form by dissociation attract water to themselves & become hydrated
- The number of water molecules attached to an ion depend on its size & charge

Examples

Be^{2+}(r=0.35A°) + $4H_2O$ → $Be(H_2O)_4^{2+}$(hydrated)

Al^{3+}(r=0.51A°) + $6H_2O$ → $Al(H_2O)_6^{3+}$ (hydrated)

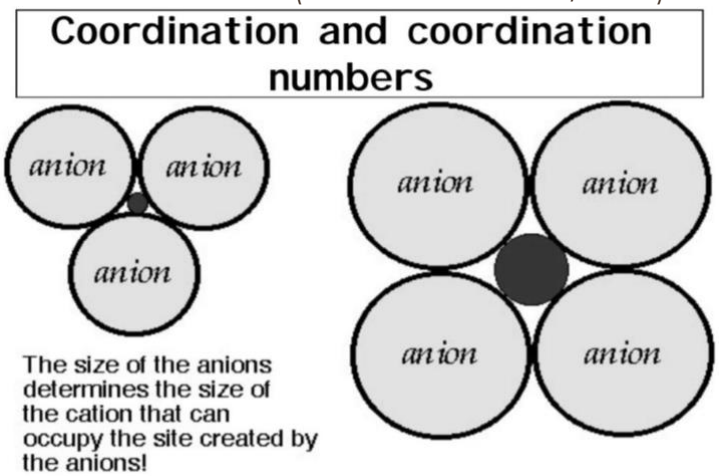
- the water is able to dissolved compounds having ionic bonding & not effective in covalent bond

IONIC CRYSTALS & COORDINATION NUMBER

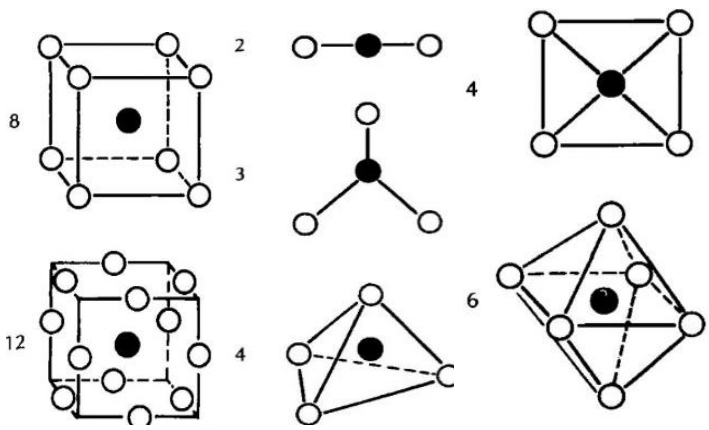
- All minerals are crystalline substance which means all have regular crystal structure
- When ions come together to form crystals, they satisfy the electrostatic requirement dictated the electrostatic bond (F) that is given by coulomb law

$$F = \frac{e1xe2}{r^2}$$

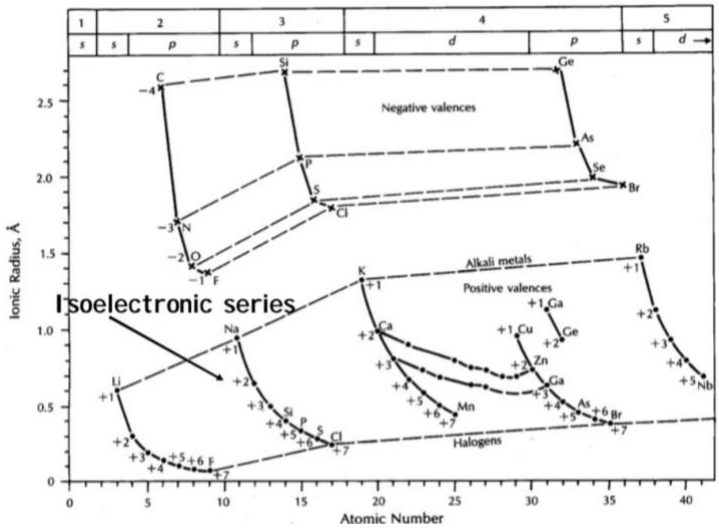
- **Coordination number:** is the number of anions that surrounded cation
  - Coordination number controled by the size of cation & anion (radius ratio of cation/anion)



Radius ratio (RR)	CN	Arrangement
< 0.155	2	Linear
0.155 – 0.225	3	Trigonal planar
0.225 – 0.414	4	Tetrahedral
0.414 – 0.732	4	Square planar
0.414 – 0.732	6	Octahedral
0.732 – 1.000	8	Body-Centered Cubic
> 1.000	12	Edge-Centered Cubic



- **Isoelectronic series**: different ions with same number of electrons (sequence of ions in which the charge increases with increasing atomic number & contains the same number of electrons)



- Some ions can have ionic radii same as other ions & this most important requirement substitution

Examples

IR of Na^+, Ca^{2+}, Cd^{2+}+, Y^{3+}+, Ti^{3+}, Th^{4+}= 1A° (CN = 6)

IR of Hf^{4+} & Zr^{4+} ≈ 0.80A° (6-fold coordination)

IR of Fe^{3+}, Co^{3+}+, & Ni^{3+} ≈ 0.65A° (CN = 6)

- The ionic radii of isoelectronic series decrease with increasing atomic number for cation & anion
- The radii of ions with the same charge increase with increasing Z (downward in the periodic table)
- The radii of ions of the same element decrease with +ve charge & increase with -ve charge
- The radii of ions with the charge +2 & +3 among the transition metals of 4 period decrease with increasing Z, by implying a contraction of the electron cloud as the 3d orbitals are filled

IONIC SUBSTITUTIONS IN A CRYSTALS

- **Goldschmidt Rules of substitution:**
  1. ***Ionic radii:*** substitution can be occur if radii of an ions differ by ≤ ±15%
  2. ***Charge:*** substitution can be occur if radii of an ions are the same or differ by ≤ ±1% with provided electrical neutrality, & if the difference > ±1 substitution is less intense
  3. ***Ionic potential (IP = charge/size):*** When two ions occupy the same structural site, the one with higher IP form stronger bond with anions
  4. ***Electronigativity (χ):*** limited substitution, the ions should be more or less equal in χ (different χ form bonds of different ionic character)

The 4th rule was formulated to explain discrepancies arose from the other three rules

Example: Na^+ & Cu^+ are monovalent & identical in size so according to the 1st & 2nd rules they should be substitute extensively in $NaAlSi_3O_8$ & NaCl, but this substitution does not take place due to Δχ (Δχ = 1.0)

Example: Can Th^{4+} substitute for Ce^{3+} in monazite ($CePO_4$)? (Hint. It's a COUPLED SUBSTITUTIONS)

1st: $IR_{Th^{4+}}$ = 1.17Å, $IR_{Ce^{3+}}$ = 1.23Å, ΔIR = 5.0% ☑

2nd: Δcharge between Th^{4+} & Ce^{3+} = 1 ☑

3rd: $IP_{Th^{4+}}$ = 3.42, $IR_{Ce^{3+}}$ = 2.44, $IP_{Th^{4+}} > IR_{Ce^{3+}}$ ☑

4th: $\chi_{Th^{4+}}$ = 1.3, $\chi_{Ce^{3+}}$ = 1.1, $IP_{Th^{4+}} > IR_{Ce^{3+}}$ ☑

Yes, they can be substitute, But we must have a coupled substitution to maintain neutrality:

$$Th^{4+} + Si^{4+} \rightarrow Ce^{3+} + P^{5+}$$

$$CePO_4 \rightarrow ThSiO_4$$

COMPATIBLE Vs. INCOMPATIBLE TRACE ELEMENTS

- **Incompatible elements**: tend to stay in liquid (in melt), large & highly charged to fit into common rock-forming minerals during crystallization, These elements become concentrated in melts
  - are highly concentrated in felsic rocks (e.g granite) which form by end phase of magma
  - Incompatible elements divided into 2 groups:
  1. **Large-ion lithophile elements (LIL)**: owing to large size (Rb, Cs, Sr, Ba, K…)
  2. **High-field strength element (HFSE)**: owing to high charge (Zr, Hf, Ta, Nb, Th, U, Mo, W…)
- **Compatible elements:** Elements that fit easily into rock-forming minerals (Cr, V, Ni, Co, Ti…)
- The different ways in which the ions partitioned between solid & liquid phases are described by:
  1) **Camouflage**: when the minor element has the same charge & ionic radius as major element

Example: Hf^{4+} (0.79Å) commonly found in the mineral zircon $ZrSiO_4$ replacing Zr^{4+} (0.80 Å)

  2) **Capture**: when a minor element enters a crystal preferentially because it has a higher ionic potential than ion of the major element

Example: feldspar captures Ba^{2+} (1.44Å) or Sr^{2+}(1.21Å) by K^+ (1.46Å), the replacement of K accompanied by substitution of Al for Si

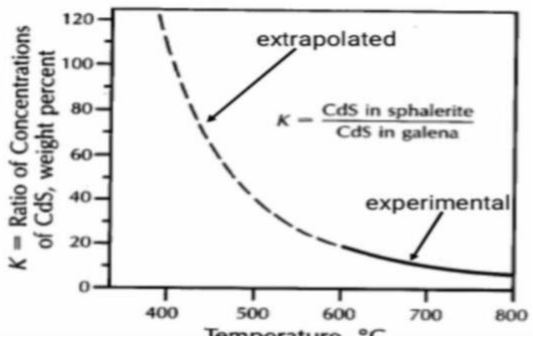
  3) **Admission**: the entry of ion that has a lower IP than the major it is replacing because it has lower charge or a larger radius, or both

Example: K^+(1.46Å) replaced by Rb^+(1.57Å) in K-feldspar, Ca^{2+}(1.08Å) by Sr^{2+}(1.21Å) in calcite & Cl^-(1.72Å) by Br^-(1.88Å) in chlorides

- **Distribution coefficient (D = Cx/Cl)**: concentration of minor element in a crystals / concentration of in a melt at equilibrium (where T is suitable)

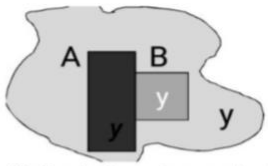
Substitution	Occur when	D
Camouflag	Charge & size are equal	= 1
Capture	IP of minor < IP of major	> 1
Admissio	IP of minor > IP of major	< 1

- **Geothermometer**: Distribution coefficient is useful in known the environment of crystallization (T-P)
  - ➢ D is determined experimentally
  - ➢ D are dependent on T, P, & composition of the phases, so used to estimate temperature of formation of coexisting minerals



A geothermometer based on the distribution of CdS between spalerite and galena

$$D_A = \left(\frac{C_y^x}{C_y^l}\right)_A \; ; \; D_B = \left(\frac{C_y^x}{C_y^l}\right)_B$$



The ratio of the distribution coefficients for element y is:

$$\frac{D_A}{D_B} = \frac{(C_y^x)_A}{(C_y^x)_B} = K = \text{constant.}$$

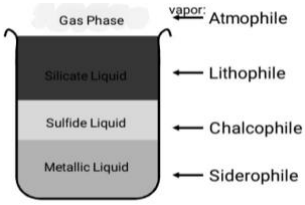
Example:

Replacement of Zn2+ (0.68 Angstrom, IV coordination) in ZnS and Pb2+ (1.26 angstrom, six fold coordination) in PbS by Cd2+ (0.88 Ansgtrom, IV coordination). The electronegativities of the three elements are very similar and all form bonds with sulphur up to 85% covalent.

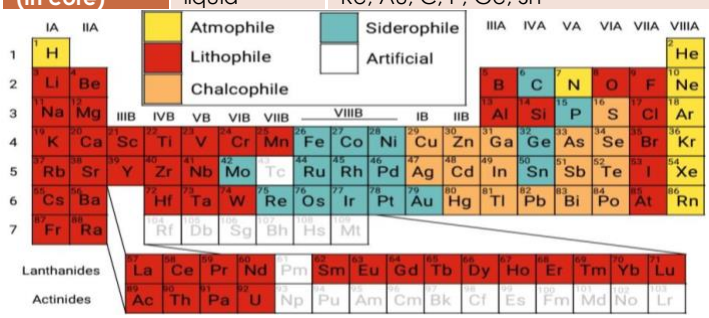
Y = mx + b ; the slope **(m) = 2080 – 0.0264 P** and the intercept on the y-axis is **b = -1.08 .**

GEOCHEMICAL AFFINITY

- **Geochemical affinity**: geochemical classification of elements, & also called Goldschmidt classification
- defined by examining ore smelting slag &meteorite
- elements are divided according to how they partition between coexisting silicate liquid, sulfide liquid, metallic liquid, & gas phase



Geochemical Affinity Classifications		
Atmophile	Gas	H, He, N, Noble gases
Lithophile (in crust)	Silicate liquid	IA, IIA, Halogens, Lanthanides, B, O, Al, Si, Sc, Ti, V, Cr, Mn, Y, Zr, Nb, Hf, Ta, Th, U
Calcophile (in mantle)	Sulfide liquid	Cu, Zn, Ga, Ag, Cd, In, Hg, Tl, As, S, Sb, Se, Pb, Bi, Te
Siderophile (in core)	Metallic liquid	Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt, Mo, Re, Au, C, P, Ge, Sn



Classification of silicate minerals			
Class	Anion	Si:O	Example
Neso	SiO_4^{4-}	1:4	Fayalite Fe_2SiO_4
Soro	$Si_2O_7^{6-}$	2:7	Akermanite $Ca_2MgSi_2O_7$
Cyclo	SiO_3^{2-}	1:3	Benitoite $BaTiSi_3O_9$
Ino single	SiO_3^{2-}	1.3	Enstatite $MgSiO_3$
Ino double	$Si_4O_{11}^{6-}$	4:11	Anthophylliite$Mg_7Si_8O_{22}(OH)_2$
Phyllo	$Si_2O_5^{2-}$	2:5	Kaolonite $Al_2Si_2O_5(OH)_4$
Tekto	SiO_2	1:2	SiO_2

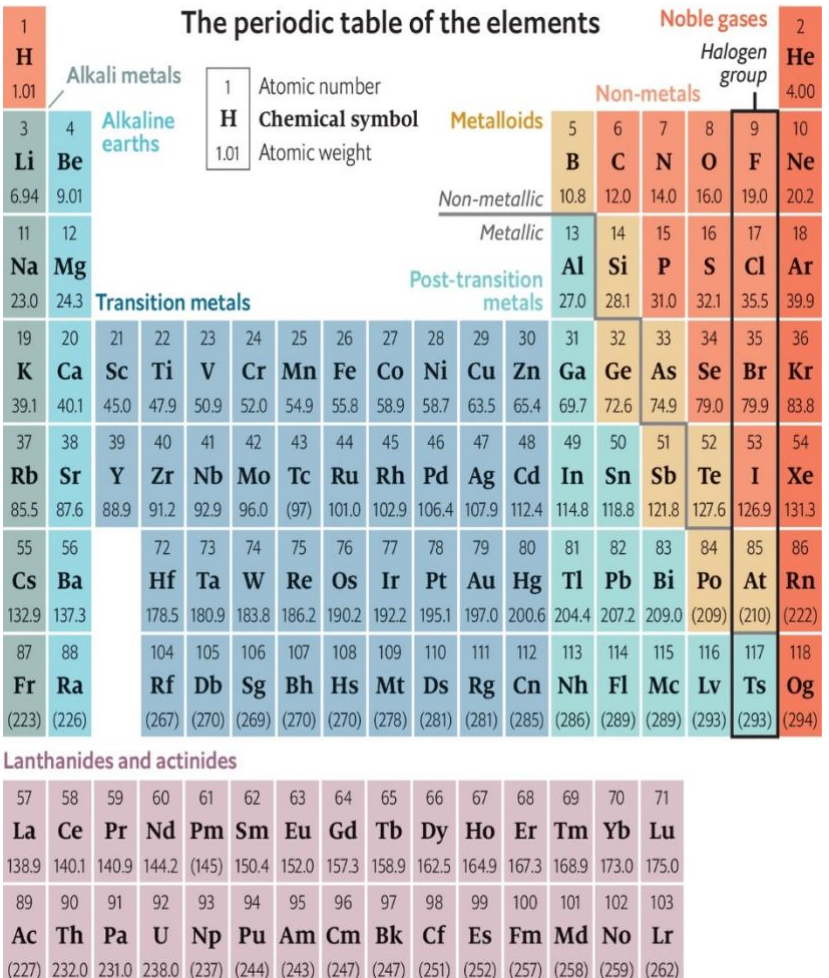
Table 7.1 First Ionization Potentials and Electronegativities of the Elements

Z	Element	First ionization potential,[a] eV	Electronegativity[b]	Z	Element	First ionization potential,[a] eV	Electronegativity[b]
1	H	13.598	2.1	48	Cd	8.993	1.7
2	He	24.587		49	In	5.786	1.7
3	Li	5.392	1.0	50	Sn	7.344	1.8
4	Be	9.322	1.5	51	Sb	8.641	1.9
5	B	8.298	2.0	52	Te	9.009	2.1
6	C	11.260	2.5	53	I	10.451	2.5
7	N	14.534	3.0	54	Xe	12.130	
8	O	13.618	3.5	55	Cs	3.894	0.7
9	F	17.422	4.0	56	Ba	5.212	0.9
10	Ne	21.564		57	La	5.577	1.1
11	Na	5.139	0.9	58	Ce	5.47	1.1
12	Mg	7.646	1.2	59	Pr	5.42	1.1
13	Al	5.986	1.5	60	Nd	5.49	1.2
14	Si	8.151	1.8	61	Pm	5.55	
15	P	10.486	2.1	62	Sm	5.63	1.2
16	S	10.360	2.5	63	Eu	5.67	
17	Cl	12.967	3.0	64	Gd	6.14	1.1
18	Ar	15.759		65	Tb	5.85	1.2
19	K	4.341	0.8	66	Dy	5.93	
20	Ca	6.113	1.0	67	Ho	6.02	1.2
21	Sc	6.54	1.3	68	Er	6.10	1.2
22	Ti	6.82	1.5	69	Tm	6.18	1.2
23	V	6.74	1.6	70	Yb	6.254	1.1
24	Cr	6.766	1.6	71	Lu	5.426	1.2
25	Mn	7.435	1.5	72	Hf	7.0	1.3
26	Fe	7.870	1.8	73	Ta	7.89	1.5
27	Co	7.86	1.8	74	W	7.98	1.7
28	Ni	7.635	1.8	75	Re	7.88	1.9
29	Cu	7.726	1.9	76	Os	8.7	2.2
30	Zn	9.394	1.6	77	Ir	9.1	2.2
31	Ga	5.999	1.6	78	Pt	9.0	2.2
32	Ge	7.899	1.8	79	Au	9.225	2.4
33	As	9.81	2.0	80	Hg	10.437	1.9
34	Se	9.752	2.4	81	Tl	6.108	1.8
35	Br	11.814	2.8	82	Pb	7.416	1.8
36	Kr	13.999		83	Bi	7.289	1.9
37	Rb	4.177	0.8	84	Po	8.42	2.0
38	Sr	5.695	1.0	85	At		2.2
39	Y	6.38	1.3	86	Rn	10.748	
40	Zr	6.84	1.4	87	Fr		0.7
41	Nb	6.88	1.6	88	Ra	5.279	0.9
42	Mo	7.099	1.8	89	Ac	6.9	1.1
43	Tc	7.28	1.9	90	Th		1.3
44	Ru	7.37	2.2	91	Pa		1.5
45	Rh	7.46	2.2	92	U		1.7
46	Pd	8.34	2.2	93	Np		1.3
47	Ag	7.576	1.9	94	Pu	5.8	1.3

Table 5.2 Electronic Structure and Valences of the Elements

Z[a]	Element	Electronic structure	Valences
1	Hydrogen	$1s^1$	+1, −1
2	Helium	$1s^2$	0
3	Lithium	$1s^2 2s^1$	+1
4	Beryllium	$1s^2 2s^2$	+2
5	Boron	$1s^2 2s^2 2p^1$	+3
6	Carbon	$1s^2 2s^2 2p^2$	+4, +2, −4
7	Nitrogen	$1s^2 2s^2 2p^3$	+5, +4, +3, +2, −3
8	Oxygen	$1s^2 2s^2 2p^4$	+6, −2
9	Fluorine	$1s^2 2s^2 2p^5$	+7, −1
10	Neon	$1s^2 2s^2 2p^6$	0
11	Sodium	$[Ne]3s^1$	+1
12	Magnesium	$[Ne]3s^2$	+2
13	Aluminum	$[Ne]3s^2 3p^1$	+3
14	Silicon	$[Ne]3s^2 3p^2$	+4, −1
15	Phosphorus	$[Ne]3s^2 3p^3$	+5, +4, +3, −3
16	Sulfur	$[Ne]3s^2 3p^4$	+6, +4, +2, −2
17	Chlorine	$[Ne]3s^2 3p^5$	+7, +5, +3, +1, −1
18	Argon	$[Ne]3s^2 3p^6$	0
19	Potassium	$[Ar]4s^1$	+1
20	Calcium	$[Ar]4s^2$	+2
21	Scandium	$[Ar]3d^1 4s^2$	+3
22	Titanium	$[Ar]3d^2 4s^2$	+4, +3
23	Vanadium	$[Ar]3d^3 4s^2$	+5, +4, +3, +2
24*	Chromium	$[Ar]3d^5 4s^1$	+6, +3, +2
25	Manganese	$[Ar]3d^5 4s^2$	+7, +6, +4, +3, +2
26	Iron	$[Ar]3d^6 4s^2$	+3, +2
27	Cobalt	$[Ar]3d^7 4s^2$	+3, +2
28	Nickel	$[Ar]3d^8 4s^2$	+3, +2
29*	Copper	$[Ar]3d^{10} 4s^1$	+2, +1
30	Zinc	$[Ar]3d^{10} 4s^2$	+2
31	Gallium	$[Ar]3d^{10} 4s^2 4p^1$	+3, +1
32	Germanium	$[Ar]3d^{10} 4s^2 4p^2$	+4, +2
33	Arsenic	$[Ar]3d^{10} 4s^2 4p^3$	+5, +3, −3
34	Selenium	$[Ar]3d^{10} 4s^2 4p^4$	+6, +4, −2
35	Bromine	$[Ar]3d^{10} 4s^2 4p^5$	+7, +5, +1, −1
36	Krypton	$[Ar]3d^{10} 4s^2 4p^6$	0
37	Rubidium	$[Kr]5s^1$	+1
38	Strontium	$[Kr]5s^2$	+2
39	Yttrium	$[Kr]4d^1 5s^2$	+3
40	Zirconium	$[Kr]4d^2 5s^2$	+4
41	Niobium	$[Kr]4d^3 5s^2$	+5, +3
42*	Molybdenum	$[Kr]4d^5 5s^1$	+6, +5, +4, +3, +2
43	Technetium	$[Kr]4d^5 5s^2$	+7
44	Ruthenium	$[Kr]4d^6 5s^2$	+8, +6, +4, +3, +2
45	Rhodium	$[Kr]4d^7 5s^2$	+4, +3, +2
46	Palladium	$[Kr]4d^8 5s^2$	+4, +2
47*	Silver	$[Kr]4d^{10} 5s^1$	+1
48	Cadmium	$[Kr]4d^{10} 5s^2$	+2
49	Indium	$[Kr]4d^{10} 5s^2 5p^1$	+3, +1
50	Tin	$[Kr]4d^{10} 5s^2 5p^2$	+4, +2
51	Antimony	$[Kr]4d^{10} 5s^2 5p^3$	+5, +3, −3
52	Tellurium	$[Kr]4d^{10} 5s^2 5p^4$	+6, +4, −2
53	Iodine	$[Kr]4d^{10} 5s^2 5p^5$	+7, +5, +1, −1
54	Xenon	$[Kr]4d^{10} 5s^2 5p^6$	0
55	Cesium	$[Xe]6s^1$	+1
56	Barium	$[Xe]6s^2$	+2
57	Lanthanum	$[Xe]5d^1 6s^2$	+3
58*	Cerium	$[Xe]4f^2 5d^0 6s^2$	+3, +4
59	Praseodymium	$[Xe]4f^3 5d^0 6s^2$	+3,+4
60	Neodymium	$[Xe]4f^4 5d^0 6s^2$	+3
61	Promethium	$[Xe]4f^5 5d^0 6s^2$	+3
62	Samarium	$[Xe]4f^6 5d^0 6s^2$	+3, +2
63	Europium	$[Xe]4f^7 5d^0 6s^2$	+3, +2
64*	Gadolinium	$[Xe]4f^7 5d^1 6s^2$	+3
65	Terbium	$[Xe]4f^9 5d^0 6s^2$	+3, +4
66	Dysprosium	$[Xe]4f^{10} 5d^0 6s^2$	+3
67	Holmium	$[Xe]4f^{11} 5d^0 6s^2$	+3
68	Erbium	$[Xe]4f^{12} 5d^0 6s^2$	+3
69	Thullium	$[Xe]4f^{13} 5d^0 6s^2$	+3, +2
70	Ytterbium	$[Xe]4f^{14} 5d^0 6s^2$	+3, +2
71	Lutetium	$[Xe]4f^{14} 5d^1 6s^2$	+3
72	Hafnium	$[Xe]4f^{14} 5d^2 6s^2$	+4
73	Tantalum	$[Xe]4f^{14} 5d^3 6s^2$	+5
74	Tungsten	$[Xe]4f^{14} 5d^4 6s^2$	+6, +5, +4, +3, +2
75	Rhenium	$[Xe]4f^{14} 5d^5 6s^2$	+7, +6, +4, +2, −1
76	Osmium	$[Xe]4f^{14} 5d^6 6s^2$	+8, +6, +4, +3, +2
77	Iridium	$[Xe]4f^{14} 5d^7 6s^2$	+6, +4, +3, +2
78*	Platinum	$[Xe]4f^{14} 5d^9 6s^1$	+4, +2
79	Gold	$[Xe]4f^{14} 5d^{10} 6s^1$	+3, +1
80	Mercury	$[Xe]4f^{14} 5d^{10} 6s^2$	+2, +1
81	Thallium	$[Xe]4f^{14} 5d^{10} 6s^1 6p^1$	+3, +1
82	Lead	$[Xe]4f^{14} 5d^{10} 6s^2 6p^2$	+4, +2
83	Bismuth	$[Xe]4f^{14} 5d^{10} 6s^2 6p^3$	+5, +3
84	Polonium	$[Xe]4f^{14} 5d^{10} 6s^2 6p^4$	+4, +2
85	Astatine	$[Xe]4f^{14} 5d^{10} 6s^2 6p^5$	+7, +5, +3, +1, −1
86	Radon	$[Xe]4f^{14} 5d^{10} 6s^2 6p^6$	0
87	Francium	$[Rn]7s^1$	+1
88	Radium	$[Rn]7s^2$	+2
89	Actinium	$[Rn]6d^1 7s^2$	+3
90	Thorium	$[Rn]5f^0 6d^2 7s^2$	+4
91*	Protactinium	$[Rn]5f^2 6d^1 7s^2$	+5,+4
92	Uranium	$[Rn]5f^3 6d^1 7s^2$	+6, +5, +4, +3
93	Neptunium	$[Rn]5f^4 6d^1 7s^2$	+6,+5, +4, +3
94	Plutonium	$[Rn]5f^6 6d^0 7s^2$	+6, +5, +4, +3
95	Americium	$[Rn]5f^7 6d^0 7s^2$	+6, +5, +4, +3
96	Curium	$[Rn]5f^7 6d^1 7s^2$	+3

*The electron configuration of starred elements is irregular.



PROBLEMS

What do the elements of each of the following groups have in common (use the periodic table)

B, Al, Ga, & In

$[B]_5 = [He]_2 2s^2 2p^1$ $[Al]_{13} = [Ne]_{10} 3s^2 3p^1$

$[Ga]_{31} = [Ar]_{18} 3d^{10} 4s^2 4p^1$ $[In]_{49} = [Kr]_{36} 3d^{10} 5s^2 5p^1$

All with s^2p^1 valence electronic configurations

+3 is the most common valence state

Be, Mg, Ca, Sr, Ba, & Ra

$[Be]_4 = [He]_2 2s^2$ $[Mg]_{12} = [Ne]_{10} 3s^2$

$[Ca]_{20} = [Ar]_{18} 4s^2$ $[Sr]_{38} = [Kr]_{36} 5s^2$

$[Ba]_{56} = [Xe]_{54} 6s^2$ $[Ra]_{88} = [Rn]_{86} 7s^2$

All with s^2 valence electronic configurations

+2 is the most common valence state

N, P, As, Sb, & Bi

$[N]_7 = [He]_2 2s^2 2p^3$ $[P]_{15} = [Ne]_{10} 3s^2 3p^3$ $[As]_{33} = [Ar]_{18} 3d^{10} 4s^2 4p^3$

$[Sb]_{51} = [Kr]_{36} 4d^{10} 5s^2 5p^3$ $[Bi]_{83} = [Xe]_{54} 4f^{14} 5d^{10} 6s^2 6p^3$

All with s^2p^3 valence electronic configurations

±3,&+5 is the most common valence state

$K^+, Ca^{2+}, Sc^{3+}, Ti^{4+}, V^{5+}$, & Cr^{6+} **All are same as noble gasses**

write the electron formula for atom having 14e- & predict its highest +ve valence

$1s^2 2s^2 2p^6 3s^2 3p^2 = [Ne]_{10} 3s^2 3p^2 = [Si]_{14}$, +4 valence

By Table 5.2, Determine how many sequences end with a valence 0

First 6 sequence (period), which end in Noble gases [He, Ne, Ar, Kr, Xe, & Rn]

Elements having similar chemical properties tend to be associated in nature. For the following pairs of elements indicate whether or not you expect them to be associated with each other. (& for it's common ions) (K-Rb) (Al-Ge) (Sc-Cu) (S-Se) (Li-Mg)

$[K]_{19} = [Ar]_{18} 4s^1$, valence = +1 $[Rb]_{37} = [Kr]_{36} 5s^1$, valence = +1

Same configurations & valence so can associate

$K^+ = [Ar]_{18}$ (0 valence) $Rb^+ = [Kr]_{36}$ (0 valence)

As ions can be associate (same electron configurations & valence)

...

Calculate the atomic weight of magnesium

Isotopes	Relative Abundance	Mass
$^{24}_{12}Mg$	78.99%	23.985042amu
$^{25}_{12}Mg$	10.00%	24.985837amu
$^{26}_{12}Mg$	11.01%	25.982593amu

Atomic Wight = Σ(A*m) = (0.7899 x 23.985042) + (0.1 x 24.985837) + (0.1101 x 25.982593) = 24.30505 ≈ 24.31amu

Calculate the formula weight of orthoclase ($KAlSi_3O_8$)

Mw (K=39.1,Al=27,Si=28.1,O=16)

39.1 + 27+ (3x28.1)+(8x16) = 278.4g/mol

How many moles of Na^+ are present in 1L of an aqueous solution of Na_2SO_4 containing 4.760g of the compound?

Mw (Na=23.0, S=32.1,O=16.0)

$Mw_{Na_2SO_4}$ = 2x23 + 32.1 + 4x16 = 142.1g/mol

$Na_2SO_4 \rightarrow 2Na^+ + SO_4^{2-} \rightarrow 1molNa_2SO_4 \rightarrow 2molNa^+$

$2n_{Na_2SO_4} = n_{Na^+} \rightarrow n_{Na_2SO_4} = m/Mw = 0.0335mol$

$n_{Na} = 2n_{Na_2SO_4}$ = ½0.0335mol = 0.0670mol

Calculate wt of 1atom ^{238}U in g (mass of isotope = 238.050784amu)

Av = 6.022045×10^{23} atoms/mol

Weight = mass/Av

238.050784(g/mol)/6.022045×10^{23}(atoms/mol)

= 3.953×10^{-22}g/atom

How many atoms of iron are present in 5.00g of (Fe_2O_3)?

Mw (Fe = 55.8, O = 16.0) → $Mw_{Fe_2O_3}$ = 2x55.8 + 3x16.0 = 159.6g/mol

$Fe_2O_3 \rightarrow 2Fe^{3+} + 3O^{-2} \rightarrow 1molFe_2O_3 \rightarrow 2molFe^{3+}$

$n_{Fe^{3+}} = 2n_{Fe_2O_3}$= 2x5.00mol/159.6= 0.0627mol

Atoms = $n_{Fe^{3+}}$ x Av = 3.773×10^{22}

Calculate concentration of Cr in chromite $FeCr_2O_4$

Mw (Fe = 55.8, Cr = 52.0, O = 16.0)

$Mw_{FeCr_2O_4}$ = 55.8 + 2x52.0 + 4x16.0 = 223.8

$FeCr_2O_4 \rightarrow Fe^{2+} + 2Cr^{+} + 4O^{-2}$

$1mol_{FeCr_2O_4} \rightarrow 2mol_{Cr^+}$ so [Cr] = $2xMw_{Cr^+}/Mw_{FeCr_2O_4}$

[Cr] = wt% = (2x52.0/223.8)100%= 46.5%

If the conc. of SO_4^{2-} = 2.5 x 10^{-3} mol/L, how many grams of SO_4^{2-} are present in one liter?

Mw (S =32.1, O = 16.0), $Mw_{SO_4^{2-}}$ = 96.1g/mol

n_{solute} = Molarity x $V_{solution}$ = 2.5 x 10^{-3} mol

m = n x Mw = 2.5x10^{-3} x 96.1 = 0.420g

[SO_4^{2-}] =m/L= 0.420g/1L = 0.420$g_{SO_4^{2-}}$/L

A solution of $A1_2(SO_4)_3$ contains 2x10^{-4}mol/L of Al^{3+}, How many grams of SO_4^{2-} does it contain per liter?

Mw (Al = 27.0, S = 32.1, O = 16.0)

Mw ($A1_2(SO_4)_3$ = 342.3, SO_4 = 96.1)

$A1_2(SO_4)_3 \rightarrow 2Al^{3+} + 3SO_4^{2-}$

$½n_{Al^{3+}} = ⅓n_{SO_4^{2-}} \rightarrow ⅔n_{SO_4^{2-}} = n_{Al^{3+}}$

$n_{SO_4^{2-}}$ = 3x2x10^{-4}/2 = 3.0x10^{-4}mol/L

$m_{SO_4^{2-}}$ = 3.0x10^{-4}x96.1 = 0.0288g/L

Determine %ionic & %covalent character of: NaCl, $FeCl_2$, CuCl, $A1C1_3$, & $CC1_4$ (χ: Cl = 3.0, Na = 0.9, Fe = 1.8, Cu = 1.9, Al = 1.5, C = 2.5)

Δχ	0.5	1.1	1.2	1.5	2.1
Ionic%	6%	26%	30%	43%	67%

NaCl = χCl - χNa = 3.0 – 0.9 = 2.1 → 67%ionic

$FeCl_2$ = χCl - χFe = 3.0 – 1.8 = 1.2 → 30%ionic

CuCl = χCl - χCu = 3.0 – 1.9 = 1.1 → 26%ionic

$AlCl_3$ = χCl - χAl = 3.0 – 1.5 = 1.5 → 43%ionic

CCl_4 = χCl - χC = 3.0 – 2.5 = 0.5 → 6%ionic

Covalent character = 100% - ionic character

Write an equation to represent the dissociation of **$(NH_4)_2SO_4$ into ions in an aqueous solution**

$(NH_4)_2SO_4 \rightarrow NH_{3(g)} + 2H^+_{(aq)} + SO_4^{2-}{}_{(aq)}$

The bond NH_4–SO_4 are ionic bond (more solube) whereas S-O are covalent(less solube)

Calculate CN for Ca^{2+} & Sr^{2+} relative to O^{-2}, & use the result to predict substitution of Ca^{2+} by Sr^{2+} (Ca = 1.18Å, Sr = 1.21Å, O = 1.32Å)

Radius ratio (RR)	CN	Arrangement
< 0.155	2	Linear
0.155 – 0.225	3	Trigonal planar
0.225 – 0.414	4	Tetrahedral
0.414 – 0.732	4	Square planar
0.414 – 0.732	6	Octahedral
0.732 – 1.000	8	Body-Centered Cubic
> 1.000	12	Edge-Centered Cubic

RR_{Ca-O} = 1.18Å/1.32Å = 0.894 → CN = 8

RR_{Sr-O} = 1.21Å/1.32Å = 0.917 → CN = 8

Substitution can occur

Hg^+ can replace Sr^{2+} in ($SrCO_3$)?

1st: IR_{Hg} = 1.05Å, IR_{Sr} =1.21Å[Avg],ΔIR=13% ☑

2nd: Δcharge = 1 ☑

3rd: IP_{Hg} = 0.952, IR_{Sr} = 1.65, $IP_{Hg} < IP_{Sr}$ ✗

Sr making stronger bond with CO_3

4th: $χ_{Hg}$ = 1.9, $χ_{Sr}$ = 1, Δχ = 0.9 ✗

There are differences in binding character due to highly differences in χ → cannot occur

Li^+ & Mg^{2+} have similar radii & χ, but Li+ does not replace Mg^{2+} in olivine. Explain the reason for this occurrence & suggest another host mineral for Li^+ in which it does replace Mg^{2+}

- **Li is incompatible elements (Large-ion lithophile elements LIL) tend to stay in liquid magma**
- **The ionic potential of Mg is very larger than of Li (2 times smaller) so Mg make stronger chemical bond with silica (IP = charge / radii)**

$IP_{Li} = 1 / R_{Li}$, $IP_{Mg} = 2 / R_{Mg}$

$R_{Li} \approx R_{Mg} \rightarrow IP_{Li} = 1/X$, $IP_{Mg} = 2/X$

$IP_{Li}/IP_{Mg} \approx ½ \rightarrow 2IP_{Li} \approx IP_{Mg}$

- **Mg^{2+}can be substitute easly by Fe^{2+} becouse the charge are equal, & radii also nearly equal so the ionic potentials (IP = charge / radii) are the same**

Chapter Five
Aqueous Geochemistry

- **There are 2 type of chemical reactions:**
  - **Kinetic reactions:** Continuous raction
  - **Equilibrium reactions:** Dynamic or reversable reaction (forward & backward)

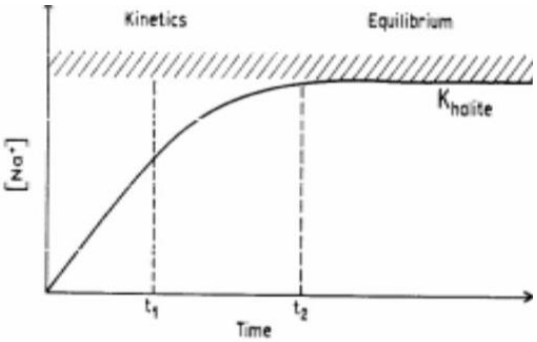
Example: Chemical reactions & equilibria

As salt (halite NaCl) dissolved in water, The concentration of Na^+ increase rapidly & then reaches equilibrium, solution becomes saturated with Na^+

$NaCl(s) \rightarrow Na^+ + Cl^-$ forward reaction

$Na^+ + Cl^- \rightarrow NaCl(s)$ backward reaction

$NaCl(s) \leftrightarrow Na^+ + Cl^-$ equilibrium (saturation)



The reaction doesn't stop at equilibrium, but rate of forward reaction become = backward

- **Solubility**: is the amount of a compound that dissolves to form a saturated solution

$$Solubility = \frac{mass\ of\ solute\ in\ gram[m]}{volume\ of\ solution\ in\ L[V]}$$

Example: $CaCO_3 + 2HCl \rightarrow Ca^{2+} + 2Cl^- + H_2O + CO_2$

When this reaction takes place in contact with the atmosphere it will not achieve equilibrium, becouse CO_2 constantly goes into the atmosphere

حتى يبقى التفاعل متزن يجب ان يكون في نظام مغلق، فأزالة او اضافة شيء منه او تغيير الحالة الفيزيائية (الحرارة والضغط) يؤدي للاخلال بالاتزان بين وينزاح التفاعل باتجاه النواتج او المتفاعلات، بهذا المثال يتم ازالة ثاني اكسيد الكربون بشكل دوري الى الغلاف الجوي فلا يصل لاتزان، وحتى التفاعلات البطيئة جدا قد لا تصل لحالة الاتزان

Example as previous example The same also applies when it happens below the water table (aquafare), **because** the slowness of a reaction taking place in nature often prevents this reaction from achieving equilibrium state

- **The Law of Mass Action Assumptions:**
  - At Equilibrium The Concentrations of Products & Reactants are Constant
  - Rates of Forward Reaction (Vf) = Backward (Vb)

aA + bB → cC + dD

$$Vf = K1[A]^a[B]^b \ \&\ Vb = K2[D]^d[C]^c$$

At equilibrium : Vf = Vb

$$K = \frac{k1}{k2} = \frac{(C)^c(D)^d}{(A)^a(B)^b},\ K = \frac{k1}{k2} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

T-dependent, (X) = concentrations, [X] = Activity

[X] = γ(X), (γ<1)

- **The units of concentrations**

$$Molality\ (m) = \frac{n[of\ solute\ in\ mole]}{m[of\ solvent\ in\ Kg]}$$

$$Molarity\ (M) = \frac{n[of\ solute\ in\ mol]}{V[solution\ in\ L]}$$

$$Formality\ (F) = \frac{n[of\ solute]}{m[of\ solution\ kg]}$$

$$Normality\ (N) = \frac{n\ of\ wieght\ of\ solute}{V\ in\ L\ of\ solution}$$

Volume increase with increasing T so as T increase M, & N decreases. m & F are more accurate

$$X = \frac{-b \pm (b^2 - 4ac)^{1/2}}{2a}$$

- Conventions of The law of Mass Action:
  - Activities expressed in moles (M, F, or m)
  - Activities of pure solid (s) & liquid (l) = 1
  - Concentration of gas are in atm partial pressure
  - Reactions assumed to take place at STP (25°C, 1atm)

DISSOCIATION OF WEAK ACIDS & BASES

- Most acid in nature is a weak acid
- **Weak acid**: doesn't completely dissociate

	Arrhenius	Bronsted
Acid	releases H^+ when dissolved in water	Donates proton H^+ to another substance
Base	release OH^- when dissolved in water	accepts proton H^+ from other substanc
Note	Not satisfactory	Accepted definition

- In Geochemistry we adopt Arrhenius since we deal with aqueous solutions of electrolytes
- Strong acids release all of their H, while the weak release part of their H. The same applies to bases, expect bases that are not soluble in water like $Mg(OH)_2$ Strong acidsStrong bases

Strong acid	HCl, HNO_3, H_2SO_4…
Weak acid	CH_3COOH, H_2CO_3, H_3PO_4, H_4SiO_4
Strong base	Metal & alkaline earthy Hydroxide Lanthanum hydroxide

Weak acids	NH_4OH, $Ni(OH)_2$, $Cu(OH)_2$ hydroxides of REE (La … Lu)

- **Amphoteric**: can behave like acid or base depend on H^+ concentration in the water (Mostly transition elements Be, Al, Si, Ti, V, Fe, Co, Zn, Ag, Au, Sn, Pb, U)

Example When 0.1molCH_3COOH dissolved in 1LH_2O (γ=1) calculate concentrations of all reactants & product at equilibrium & calculate the degree of dissociation D% (K = $1.76x10^{-4}$)

	CH_3COOH	↔	$CH3COO^-$	H^+
n	1mol	↔	1mol	1mol
I	0.1m	↔	0	0
Δ	-X	↔	+X	+X
F	0.1 - X	↔	+X	+X

$K = [H^+][CH3COO^-]/[CH_3COOH] = 1.76x10^{-5}$

$K = X^2/(0.1-X) = 1.76x10^{-5}$

$\rightarrow X^2 + 1.76x10^{-5}X - 1.76x10^{-6} = 0$

$X = (-1.76x10^{-5} \pm 2.65x10^{-3})/2 = \pm 1.32\ x10^{-3}$

$[H^+] = [CH3COO^-] = X = 1.32\ x10^{-3}m$

$[CH_3COOH] = 0.1 - X = 0.0987m \approx 0.1m$

$$Degree\ of\ dissocation\ (D\%) = \frac{X}{[reactant]i}$$

$D\% = (1.32\ x10^{-3}/0.1)\ x\ 100\% = 1.32\%$

- The dissociation of water into ions:

$H_2O \leftrightarrow H^+ + OH^-$; Kw at STP = $1.0x10^{-14}$

$$Kw\ at\ STP = [H^+][OH^-] = 1.0x10^{-14}$$

$$[H^+] = [OH^-] = 1.0x10^{-7}$$

$pH = -\log[H^+]$, $pX = -\log[X]$, $[H^+] = 10^{-pH}$

$pH + pOH = 14$, $pKc + pKa = 14$

$pH\ x\ pOH = 10^{-14}$, $pKc\ x\ pKa = = 10^{-14}$

Example In the previous ex calculate pH, pOH, & pK

Solution

$pH = -\log(1.32x10^{-3}) = 2.88$

$[OH-] = (1x10^{-14})/(1.32x10^{-3}) = 0.757x10^{-11}m$

$pOH = -\log[OH] = -\log(0.757x10^{-11}) = 11.2$

OR : $pOH = 14 - pH = 11.2$

$pK = -\log[1.76x10^{-4}] = 3.75$

- Concentrations (activities) are represented by expressions with -ve exponents $X = 10^{log^x}$

Example

$$2.5x10^{-5} = 10^{log^{2.5x10^{-5}}} = 10^{-4.6}$$

- **Diprotic acid:** Weak acids dissociate ***stepwise***
- The calculation of activities can be done with 2 procedures: ***stepwise*** & ***simultaneous***

Example If solution contains 0.1molH dissolved in 1LH_2O (if $K1=10^{-7}$, & $K2 = 10^{-12.9}$)

H_2S	↔	HS^-	H^+
0.1(0.1-≈x)	↔	+X	+X

$X^2/0.1 = 10^{-7} \rightarrow X = 10^{-4}m$, pH = 4.0

$(10^{-4})/0.1 \ll 0.1$ ☑, $D\% = 100(10^{-4})/0.1 = 0.1\%$

HS^-	↔	S^{-2} +	H^+
$10^{-4} - y$	↔	+y	$10^{-4}+y$

$(10^{-4}+y)(y)/(10^{-4}-y) = 10^{-12.9}$

$y \ll 10^{-4}$ then $10^{-4} + y = 10^{-4} - y = 10^{-4}$

$D\% = 10^{-12.9}x100/\ 10^{-4} = 10^{-6.9}\%$

H_2S stronger than HS^- because (K1>K2)

pH CONTROL OF DISSOCIATION EQUILIBRIUM

- dissociation of weak acids & bases controlled by the pH of the geochemical environment
- We can rewrite the mass action equations as:

$$[H_2S] = \frac{[HS^-][H^+]}{10^{-7}}\ \&[S^{-2}] = \frac{[HS^-]10^{-12.9}}{[H^+]} \ldots (1)$$

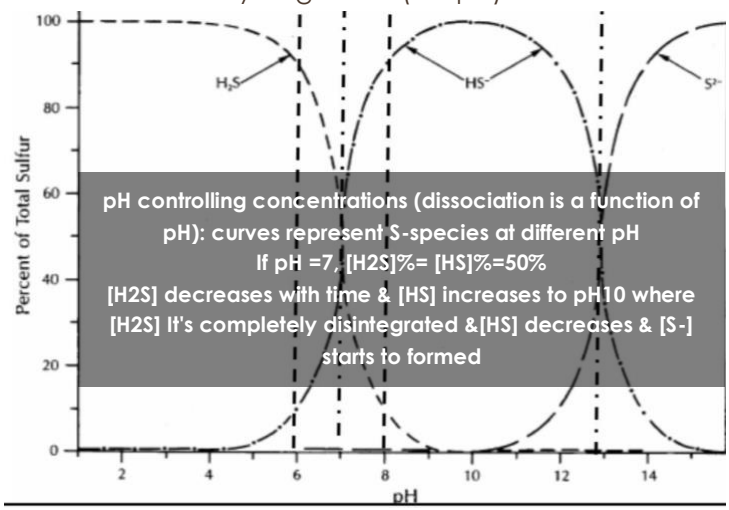
If we know the concentration of all species, then:

$[H_2S] + [HS^-] + [S^{2-}] = X$

$$\frac{[HS^-][H^+]}{10^{-7}} + [HS^-] + \frac{[HS^-]10^{-12.9}}{[H^+]} = X$$

$$[HS^-] = \frac{X}{1 + \frac{[H^+]}{10^{-7}} + \frac{10^{-12.9}}{[H^+]}} \ldots (2)$$

The activity ratios of the ions depend on the activity of hydrogen ion (i.e. pH)



Example in the previous example if the total amount of sulphur species 10^{-2} mol/L calculate the activities of three species as a function of pH (At pH = 6)

Solution $pH = 6 \rightarrow [H] = 10^{-6}$

$$[HS^-] = \frac{10^{-2}}{1 + \frac{10^{-6}}{10^{-7}} + \frac{10^{-12.9}}{10^{-6}}} = 9.1x10^{-4}$$

$$[H_2S] = \frac{9.1x10^{-4}x10^{-6}}{10^{-7}} = 9.1x10^{-3}$$

$$[S^{-2}] = \frac{9.1x10^{-4}x10^{-12.9}}{10^{-6}} = 1.1x10^{-10}$$

$[H_2S]$ the dominant species at pH=6 (90.0%) of all S-ions

SOLUBILITY OF AMORPHOUS SILICA

- Solubility of silica is **Very Low** because the **chemical bond** in silica is **very strong** (mostly to totally covalent bond & water molecules react with ionic bonding molecule & minerals)
- Metallic Oxide dissolve to produce strong base, & Non-metallic dissolve to produce weak acid

Examples $CO_2 + H_2O \rightarrow H_2CO_3$

$SO_2 + H_2O \rightarrow H_2SO_3$

$SiO_2(amorphous) + 2H_2O \rightarrow H_4SiO_4$, $K=10^{-2.74}$

- **Silicic acid (H_4SiO_4)** form mostly by chemical weathering of aluminosilicates rather than from

amorphous dissolution, because solubility of amorphous silica is very low (e.g. Olivine)

- When solubility of silica exceeded, forms amorphous silica which settles down as a ***gelatinous precipitate***
- In gelatinous precipitate the water become expelled & crystallization starts to form opal-A & opal CT (intermediate) & gives rise to cryptocrystalline ***chalcedony*** (chert,flint) & occurs as ***geodes & agate***

- **Dissociation of Silicic Acid**

H_4SiO_4	↔	$H_3SiO_4^-$	+	H^+	$K=10^{-9.7}$
$H_3SiO_4^-$	↔	$H_2SiO_4^{-2}$	+	H^+	$K=10^{-13.2}$
$H_2SiO_4^{-2}$	↔	$HSiO_4^{-3}$	+	H^+	$K=10^{-9.8}$
$HSiO_4^{-3}$	↔	SiO_4^{-4}	+	H^+	$K=10^{-13.3}$

- **Activity of silicic acid at 25°C**

$SiO_{2(s)}+2H_2O_{(l)} \rightarrow H_4SiO_{4(aq)}, K=10^{-2.74}$, $[H_4SiO_4]$ $10^{-2.74}$

  - Equilibrium is pH- independent because H ion isn't produced but T-dependent

Example degree of dissociation of silicic acid at pH = 7 calculated stepwise from the eq of the first dissociation

	H_4SiO_4	↔	$H_3SiO_4^-$	+	H^+	$K=10^{-9.7}$
i	$10^{-2.74}$	↔	0	+	0	
Δ	$10^{-2.74} - x$	↔	X	+	X	
F	$10^{-2.74}$	↔	X	+	X	

$$\frac{[H3SiO4^-]}{10^{-2.74}} = \frac{10^{-9.7}}{10^{-7}} \rightarrow [H3SiO4^-] = 10^{-5.44}$$

$$D\% = \frac{10^{-5.44}}{10^{-2.74}} x100\% = 0.19\%$$

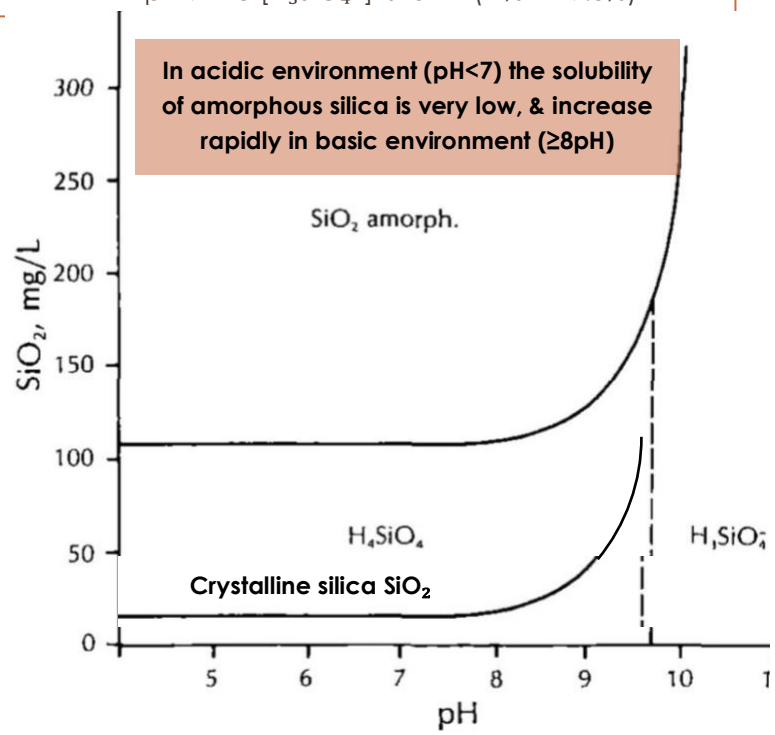
$[H_3SiO_4^-]$ at pH 7 < 500 times than H_4SiO_4 so does not contribute to the solubility of SiO_2

- **the dissociation of silicic acid is extremely low at pH < 8 & rises rapidly after that**

Example

At pH 8 the $[H_3SiO_4^-]$ is $10^{-4.15}$ (D% = 1.95%)

At pH 9 the $[H_3SiO_4^-]$ is $10^{-3.45}$ (D% = 19.5%)



- A consequence of that is the rapid increase of solubility of amorphous silica since it is based on the sum of the Si-bearing ions in solution
- The figure shows a small change in the pH (at pH>8) would result in the stabilization of SiO_2

Example decrease of 0.1 pH (8.5 to 8.4) of a saturated solution of silica deposit 1.37mg/L, This amount produce huge silica deposits when the large volumes of groundwater over a large period of time, & by convert the unit into mol/L, $25/(60.08x10^3) = 4.16x10^{-4}$ mol/L

- **Quartz has lower solubility than amorphous**

Example

SiO_2(quartz) + $2H_2O \rightarrow H_4SiO_4$, $K=10^{-4.1}$

$[H_4SiO_4]$ in contact with quartz is equal to $10^{-4.1}$m

10-4.1 equivalent to 5.9 mg/L of SiO_2 in solution

- **Silica vs Amorphous in river waters**

$SiO_{2riverwater}$ = (6.5x60.1/28.1) =13.9ppm(mg/L)

Crystalline Silic : 13.9>5.9ppm → supersaturated

Amorphous Silica:13.9<110ppm→Undersaturated

PROBLEMS

Calculate pH of HF containing 0.1mol/L.(pK 3.2)

	HF	↔	F^-	+	H^+
[Initial]	0.1m		0		0
[Δcon]	-X		+X		+X
[Final]	0.1 (0.1-x ≈x)		+X		+X

pK = 3.2 → K = $10^{-3.2}$ → X^2 = K = $10^{-3.2}$ → X = 0.025m

pH = - log[0.025] = 1.6, $D\% = \frac{0.025}{0.1} x100\% = 25\%$

Calculate the activities of all ions & the pH of a solution containing 0.1molH_3PO_4/L. (pK1 2.1, pK2 7.2, pK3 12.4)

	H_3PO_4	↔	$H_2PO_4^{-1}$	+	H^+
I	0.1m		0		0
Δ	-X		+X		+X
F	*Assumption* 0.1		+X		+X

pK = -logK → K = $10^{-2.1}$

X^2 = 0.1 x $10^{-2.1}$ → X = $[H^+]$ = $[H_2PO_4^-]$ = $10^{-1.55}$

D% = 28.2% (good *Assumption* → weak acid)

Result : $[H^+]$ = $[H_2PO_4^-]$ = $10^{-1.55}$mol/L & $[H_3PO_4]$ = 0.0718 ≈ 1.0 mol/L

$H_2PO_4^{-1}$	↔	HPO_4^{-2}	+	H^+
$10^{-1.55}$		0		$10^{-1.55}$
As. $10^{-1.55}$		+X		*As.* $10^{-1.55}$

pK = 7.2 → K = $10^{-7.2}$

$$\frac{[HPO4^{-2}]x10^{-1.55}}{10^{-1.55}} = 10^{-7.2}$$

X = $10^{-7.2}$ = $[HPO_4^{-2}]$

D% = $10^{-3.65}$% (good *Assumption* → very weak acid)

Result : $[H^+] \approx [H_2PO_4^-] \approx 10^{-1.55}$mol/L & $[HPO_4^{-2}] \approx 10^{-7.2}$ mol/L

HPO_4^{-2}	↔	PO_4^{-3}	+	H^+
$10^{-7.2}$		0		$10^{-1.55}$
-X		+X		+X
As. $10^{-7.2}$		+X		*As.* $10^{-1.55}$

pK = 12.4 → K = $10^{-12.4}$

$$\frac{[PO4^{-3}]x10^{-1.55}}{10^{-7.2}} = 10^{-12.4}$$

$[PO_4^{-3}]$ = $10^{-18.1}$

D% = $10^{-10.9}$% (good Assumption → too weak acid)

Result : $[PO_4^{-3}]$ = $10^{-18.1}$ mol/L & $[HPO_4^{-2}] \approx 10^{-7.2}$ mol/L $[H^+] \approx 10^{-1.5}$ mol/L

$[H^+]$ in all steps = $10^{-1.55}$mol/L → pH = 1.55

This acid completely disintegrates as put in water, so ΔpH neglected

Chapter Six
Salts & Their Ions

- All minerals can be considered as salts
  Salt + Water → Anions + cations (acids + bases)
- **solubility product constant Ksp** *directly proportional to the solubility*, for **aA ⇔ bB + cC**
  Ksp (at equilibrium) = $[B]^b x [C]^c$

Example Calculate $[SO_4^{2-}]$ & Calculate the amount of sulfate which dissolved in water (Ksp = 69.19)

$$Al_2(SO_4)_{3(s)} \Leftrightarrow 2Al^{3+} + 3SO_4^{2-}$$
$$2X \qquad 3X$$
$$[Al^{3+}]^2[SO_4^{2-}]^3 = (2X)^2x(3X)^3 = 108X^5 = Ksp$$
$$108X^5 = 69.19 \rightarrow X = 0.915 mol/L$$
$$[SO_4^{2-}] = 3X = 2.74 mol/L$$
0.915mol/Lx342.15g/mol = 313 gm/L of water
saturated الماء الذي يحتوي 313 جم/ل هو بحالة اتزان

- **Ion Activity Product (IAP): for aA ⇔ bB + cC**
  IAP (at any time) = $[aB]^b x [bC]^c$

Example: A solution with $5x10^{-2}$molCa^{2+} & $7x10^{-3}$ mol SO_4^{2-} are saturated with respect to Anhydrite? Ksp $10^{-4.5}$

$$CaSO_4 \Leftrightarrow Ca^{2+} + SO_4^{2-}, \text{ then } [Ca^{2+}][SO_4^{2-}] = 10^{-4.5}$$
$$IAP = 5x10^{-2}x7x10^{-3} = 3.5x10^{-4} = 10^{-3.45}$$
IAP > Ksp → solution is supersaturated with respect to anhydrite → anhydrite precipitate

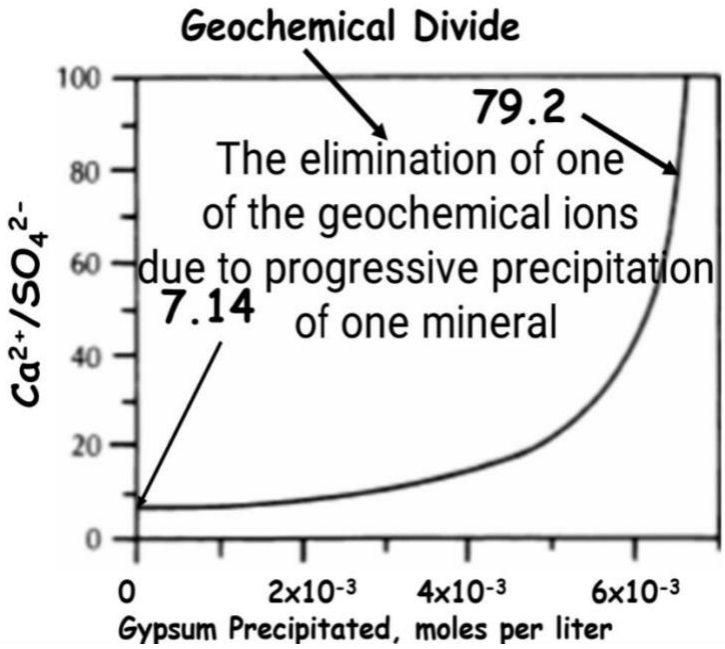
- **Saturation Index:** $SI = log^{\frac{IAP}{Ksp}}$

SI	Ksp Vs IAP	Saturation	State
0	IAP = Ksp	saturation	equilibrium
< 0	IAP < Ksp	undersaturation	Dissolution
> 0	IAP > Ksp	supersaturation	Precipitation

- Anhydrite doesn't form directly, first gypsum forms & transfers to anhydrite, so anhydrite dissolution is **irreversible reaction**

Example Calculate amount of gypsum at equilibrium from 100L of seawater (use values in previous example)

$$CaSO_4.2H_2O \Leftrightarrow Ca^{2+} + SO_4^{2-} + 2H_2O$$
$$Ksp = [Ca^{2+}][SO_4^{2-}] = 10^{-4.6}$$
If x moles of gypsum precipitate; the activities will be:
$$IAP = (5x10^{-2} - x)(7x10^{-3} - x) = 10^{-4.6}$$
$$X = 6.5x10^{-3} mol/L = 1.11 g/L = 111.0 \text{ grams } /100L$$
$$\frac{[Ca^{2+}]}{[SO4^{-2}]} before\ preceptation = \frac{5x10^{-2}}{7x10^{-3}} = 79$$
$$\frac{[Ca^{2+}]}{[SO4^{-2}]} After = \frac{3.35x10^{-2}}{5.5x10^{-4}} = 7.9$$
7.9 is at equilibrium , & This ratio continuously changes during precipitation



Example 50.0gNaCl is added to 1L solution containing 10^{-3}molAg+. Demonstrate that AgCl precipitates from solution & calculate the weight of AgCl that precipitate (γ =1, Ksp of AgCl = $10^{-9.75}$, Mw of NaCl = 58.443)

Solution $NaCl \rightarrow Na^+ + Cl^-$
$$Ag^+ + Cl^- \rightarrow AgCl \text{ (which precipitates)}$$
$$n\ NaCl = n\ Cl = 50.0/85.443 = 8.55x10^{-3}mol$$
$$IAP = [Cl][Ag] = 8.55x10^{-3}x10^{-3} = 10^{-5.067}$$
IAP > Ksp → supersaturation → AgCl precipitate
Let x = n AgCl that precipitate. At equilibrium:
$$[Ag+] = 10^{-3} - x, [Cl-] = 8.55x10^{-3} - x$$
$$(10^{-3} - x)(8.55x10^{-3} - x) = 10^{-9.75} \rightarrow X = 10^{-3}$$
$$[Ag+] = 10^{-3} - 10^{-3} = 0$$
$$[Cl-] = 8.55x10^{-3} - 10^{-3} = 7.55x10^{-3} mol/L$$
All of the Ag is removed as AgCl precipitate

COMMON ION EFFECT

Example a solution saturated with gypsum & barite

$$CaSO_4.2H_2O \Leftrightarrow Ca^{2+} + SO_4^{2-} + 2H_2O$$
$$BaSO_4 \Leftrightarrow Ba^{2+} + SO_4^{2-}، \text{ Common ion is } SO_4^{2-}$$
$$[Ca^{2+}][SO_4^{2-}] = Ksp1 = 10^{-4.6}, [Ba^{2+}][SO_4^{2}] = Ksp2 = 10^{-10}$$
$$[SO4^{-2}] = \frac{Ksp1}{[Ca^{+2}]} = \frac{Ksp2}{[Ba^{+2}]} At\ equilibrium$$
$$then: \frac{[Ca]}{[Ba]} = \frac{Ksp1}{Ksp2}$$
$$[Ca^{2+}]/[Ba^{2+}] = 25x10^4$$
If the ratio = $25x10^4$ → equilibrium
if the ratio > $25x10^4$ → [Ba] precipitate & [Ca] dissolve,
if the value < $25x10^4$ → [Ca] precipitate & [Ba] dissolved

Example For requirement of electrical neutrality:

$2(Ba^{2+}) + 2(Ca^{2+}) + (H^{+}) = 2(SO_4^{2-}) + (OH^{-})$

$$\Sigma(conc.x\,|charge|)p = \Sigma(conc.x\,|charge|)r$$

electrical neutrality = conc x charge

From the equations of dissociation constants

$$(Ca^{+2}) = \frac{Ksp1}{\gamma[SO4^{-2}]}, (Ba^{+2}) = \frac{Ksp2}{\gamma[SO4^{-2}]}$$

By Substituting in the mass balance equation & dropping the $[H^+]$ & $[OH^-]$, if γ = 1.0 we get:

$$2(SO_4^{2-}) = 2(Ba^{+2}) + 2(Ca^{+2})$$

$$(SO_4^{2-}) = \frac{10^{4.6}}{[SO_4^{2-}]} + \frac{10^{-10}}{[SO_4^{-2}]}$$

Then : $[SO_4^{2-}] = 10^{-2.3}$ mol/L

The contribution of barite to the sulphate is negligible → gypsum is able to *force barite to precipitate* when saturated solution of barite contact with gypsum → barite replace gypsum & anhydrite

Barite precipitates as both minerals dissovle & this process continues until the [Ca2+]/[Ba2+] ≈ 25 x10^4 as required by equilibrium

- Replacement of minerals occur due to introduction of a common ion into the environment force the solution to become supersaturated with respect to the less soluble compound, & The more soluble compound is replaced by the less soluble one

Example Predict the outcome of reactions that occur when a solution having $[Cd^{2+}/Pb^{2+}]$ = 25 (equiperum) come in contact with a rock containing galena PbS, Will additional galena precipitate, or dissolve? Will CdS precipitate? & What will be ratio of $[Cd^{2+}/Pb^{2+}]$ in the solution after equilibrium? (Ksp: CdS = 10^{-27}, PbS = $10^{-27.5}$)

$CdS \rightarrow Cd^{2+} + S^{-2}$, Ksp = 10^{-27}

$PbS \rightarrow Pb^{2+} + S^{-2}$, Ksp = PbS = $10^{-27.5}$

$[S^{-2}] = 10^{-27}/[Cd^{2+}] = 10^{-27.5}/[Pb^{2+}]$

$[Cd^{2+}]/[Pb^{2+}] = 10^{-27}/10^{-27.5} = 3.16$

Ratio of solution (25) > Ratio at equilibrium (3.16)

The solution is supersaturated with respect to Cd^{2+} & Undersaturated with respect to Pb^{2+}

So: PbS dissolved & CdS Precipitate according to the following reactions

$PbS_{(s)} \rightarrow Pb^{2+}_{(aq)} + S^{-2}_{(aq)}$

$Cd^{2+}_{(aq)} + S^{-2}_{(aq)} \rightarrow CdS_{(s)}$

- **Supersaturation of solutions with respect to a specific compound result from:**
  I. **Introduction of a common ion**
  II. **Change in pH** (precipitation of amorphous)
  III. **Evaporative concentration** of water
  IV. **Temperature-variation: solubility increase with rising T** (Except for carbonates, decrease)

ACTIVITIES & CONCENTRATIONS

يختلف التركيز الفعال Activity عن التركيز Concretion لوجود ايونات (-ve+, ve) وتأثير الايونات على بعضها يقلل من نشاطها

- The ions in solution don't interfere with each other, but holds true only for extremely diluted solutions
- Ions of opposite charges in a solution interact with each other, so the activities of the ions are lower than their actual concentrations
- The interaction among ions is a function of: concentration, charges, & size, & all of that is summarized in ***Debye-Hückel theory***

- ***Debye-Hückel theory***: concentrations & charges of ions in solution are expressed by ionic strength (I)

$$I = \frac{1}{2}\Sigma mz^2$$

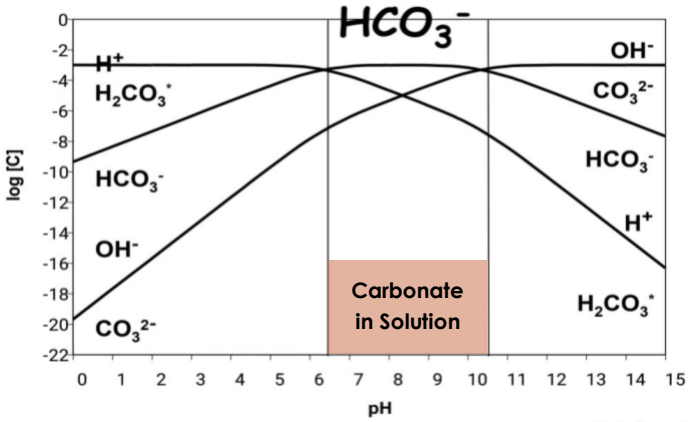
***z**: is a charge if an ion, **m**: concentration in mol/L*

From 0.001 to 0.1 in rivers & lakes, 0.7 in seawater, & up to 5 in brines

- **A full chemical analysis is needed to calculate the ionic strength for a given body of water**
  I. The ppm conc are converted to moles

$$mol = \frac{ppm\ (or\ mg)}{1000 * Mw}$$

  II. H^+ & OH^- reported if the solution is either highly acidic or basic, then they should be considered
  III. SiO_2 is neutral it does not contribute to I
  IV. Carbonates reported as HCO_3^- (dominant carbonate species at pH = 6.35 - 10.3)



EXAMPLE Calculate the ionic strength

Ions	Con [ppm]	Mw [g/mol]	Con [m]	ζ^2	m x ζ^2
HCO_3^-	116.0	61.0	$1.9x10^{-5}$	1	0.00190
SO_4^{2-}	25.5	96.1	$2.65x10^{-4}$	4	0.00106
Cl^-	10.3	35.5	$2.90x10^{-4}$	1	0.00029
NO_3^-	2.70	62.0	$4.3x10^{-5}$	1	$4.355x10^{-5}$
Ca^{2+}	34.0	40.1	$8.5x10^{-4}$	4	0.00339
Mg^{2+}	8.9	24.3	$3.7x10^{-4}$	4	0.001465
Na^+	11.9	23.0	$5.17x10^{-4}$	1	0.000517
K^+	1.90	39.1	$4.9x10^{-5}$	1	$4.859x10^{-5}$
Fe^{2+}	0.14	55.8	$2.5x10^{-6}$	4	$1.004x10^{-5}$
SiO_2	11.7	60.1	$1.95x10^{-4}$	0	0
Total					0.00872

$I = ½\Sigma(mz^2) = ½x0.00872 \approx 0.0044$

Example Find the ionic strength for a 0.1 mol of solution of $MgCl_2$

$MgCl_2 \rightarrow Mg^{2+} + 2Cl^-$

$M_{MgCl_2} = M_{Mg^{2+}} = 0.1$mol/Kg

$2M_{MgCl_2} = M_{Cl^-} = 0.2$mol/Kg

$I = ½\Sigma(Mxz^2) = ½(0.1x2^2 + 0.2x(-1)^2) = 0.6/2 = 0.3$

- The ionic strength is used in the DebyeHueckel theory to estimate the activity coefficient (γ):

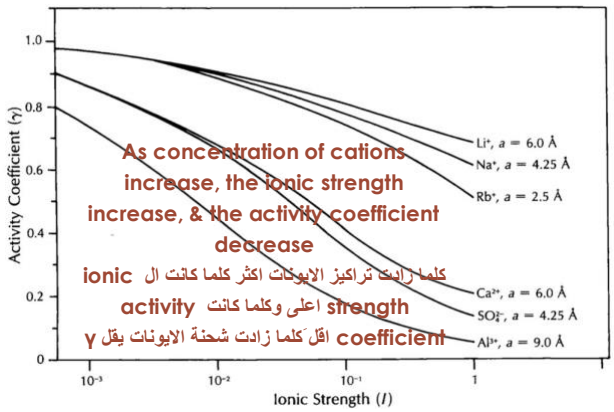
[X] = γ (X)

If I < $5x10^{-3}$ → $-log^{\gamma} = Az^2I^{½}, \gamma = 10^{-Az^2I^{½}}$

If I < 0.1 → $-log^{\gamma} = \frac{Az^2I^{½}}{1+aBI^{½}}, \gamma = 10^{-\left(\frac{Az^2I^{½}}{1+aBI^{½}}\right)}$

If I = 0.5 → $-log^{\gamma} = Az^2\left[\frac{I^{½}}{1+I^2} - 0.2I\right]$

a: effective diameter of the ion



- The interference of the ions in solution causes the solubility to increase

Example solubility of $CaSO_4$ is 5.6×10^{-3} mol/L, then Ca^{2+} concentration is (I=0.0044, γ= 0.759)

$[Ca^{2+}] = 5.6\times10^{-3}$

$[Ca^{2+}] = \gamma(Ca^{2+}) = 5.6\times10^{-3}$mol/L

$(Ca^{2+}) = 5.6\times10^{-3}/0.759 = 7.38\times10^{-3}$mol/L

The increase in solubility $=\frac{(x)-[x]}{[x]}$ = 32%

SOLUBILITY OF CALCIUM CARBONATES

- **Calcite Vs carbonic acid**

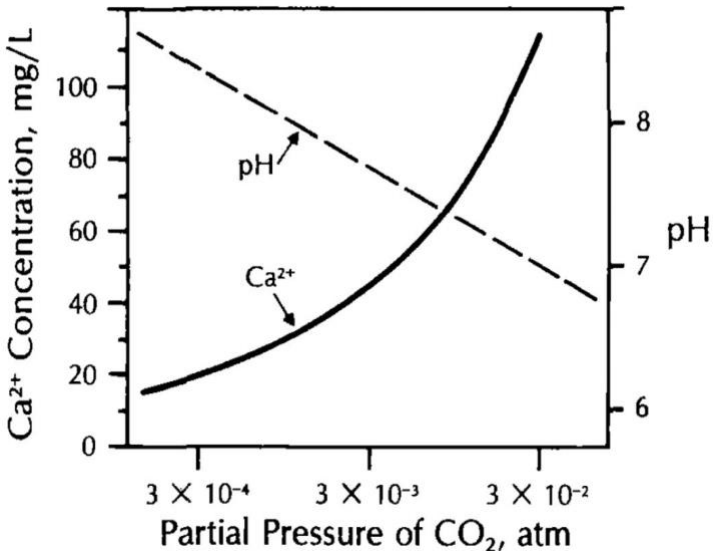
$CaCO_3 + H_2CO_3 \Leftrightarrow Ca^{2+} + 2HCO_3^-$ (pH > 8.9)

The carbonic acid is in equilibrium with CO_2

$H_2CO_{3(s)} \Leftrightarrow CO_{2(aq)}+H_2O_{(l)} \rightarrow CO_{2(aq)} \Leftrightarrow CO_{2(g)}$

With increasing partial pressure of CO_2, led to the increase the activity of H_2CO_3 & solubility of calcite

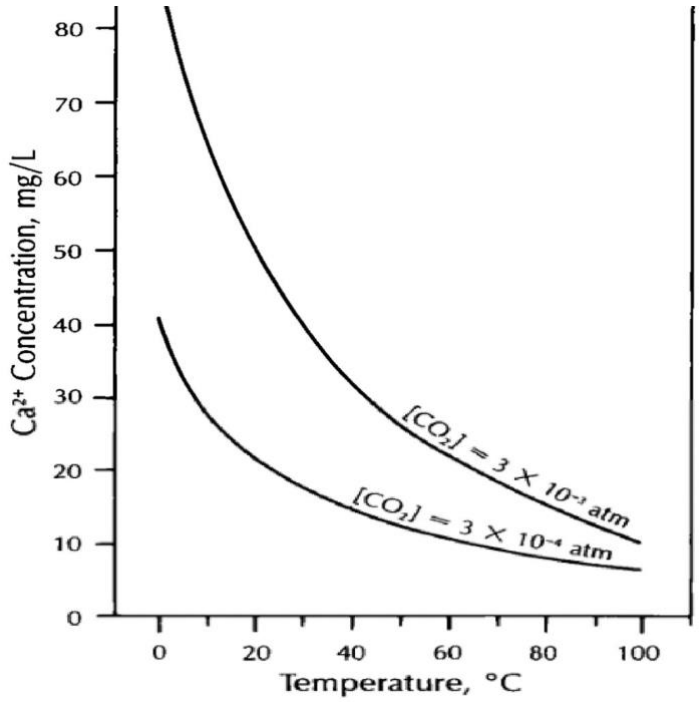
- Solubility of gas decreases with T, so in polar regions the rate of limestone precipitation < in tropical regions because CO_2 more soluble in polar regions



كلما زاد تركيز ثاني اكسيد الكربون تكون الذائبية اعلى وكلما زادت T تكون الذائبية اقل

- **The environments of limestone precipitation**: shallow water in tropical regions
- The aquatic organisms decrease the partial pressure of CO_2 during the day through the combination of CO_2 & H_2O to produce glucose ($C_6H_{12}O_6$) which led to precipitation of $CaCO_3$ (algae precipitate calcite through this mechanism & produce thinly laminated calcite mounts called stromatolites)
- The deposition of speleothems in the form of ***stalactites & stalagmites*** in the caves is also a response to changes in CO_2 partial pressure
- Calcite Solubility as a function of CO_2 pressure

One of the most common structure of calcium carbonate are Stalactites (from roof of the cave, down), Stalagmite (from floor of the cave, up) &Column(Stalactite+Stalagmite)



PROBLEMS

Q1 **Calculate the activities of Ca^{2+} & F^- & the solubility of fluorite (CaF_2) in mol/L & g/100L in water at 25°C (assuming all γ =1, pKsp = 10.4, & Mw of CaF_2 = 78.1g/mol)**

$CaF_{2(s)} \Leftrightarrow Ca^{2+}_{(aq)} + 2F^-_{(aq)}$

$(2X)^2\times X = Ksp = 10^{-10.4} \rightarrow X = 2.2\times10^{-4}$ mol/L

$[Ca^{2+}] = X = 2.2\times10^{-4}$, $[F^-] = 2X = 4.4\times10^{-4}$

$S_{CaF_2} = 2.2\times10^{-4}$mol/L = 1.72g/100L

Q2 **Calculate the ionic strengths of water in the following samples (A) & (B)**

	A [ppm]	B [ppm]	Mw [g/mol]
HCO_3^-	50.0	121	61.0
SO_4^{2-}	4.8	28	96.1
Cl^-	1.5	17	35.5
NO_3^-	0.52	1.2	62.0
Ca^{2+}	14.1	39	40.1
Mg^{2+}	3.7	8.7	24.3
Na^+	2.9	8.2	23.0
K^-	0.5	1.4	39.1
Fe^{2+}	0.36	0.03	55.8
SiO_2	4.1	2.1	60.1

Using excel sheet

	A [ppm]	Mw [g/mol]	A [mol/L]	ζ^2	$m*\zeta^2$
HCO_3^-	50	61	0.000819672	1	0.000819672
SO_4^{2-}	4.8	96.1	4.9948E-05	4	0.000199792
Cl^-	1.5	35.5	4.22535E-05	1	4.22535E-05
NO_3^-	0.52	62	8.3871E-06	1	8.3871E-06
Ca^{2+}	14.1	40.1	0.000351621	4	0.001406484
Mg^{2+}	3.7	24.3	0.000152263	4	0.000609053
Na^+	2.9	23	0.000126087	1	0.000126087
K^-	0.5	39.1	1.27877E-05	1	1.27877E-05
Fe^{2+}	0.36	55.8	6.45161E-06	4	2.58065E-05
SiO_2	4.1	60.1	6.82196E-05	0	0

I = 0.001625162

	B [ppm]	Mw [g/mol]	B [mol/L]	ζ^2	$m*\zeta^2$
HCO_3^-	121	61	0.001983607	1	0.001983607
SO_4^{2-}	28	96.1	0.000291363	4	0.001165453
Cl^-	17	35.5	0.000478873	1	0.000478873
NO_3^-	1.2	62	1.93548E-05	1	1.93548E-05
Ca^{2+}	39	40.1	0.000972569	4	0.003890274
Mg^{2+}	8.7	24.3	0.000358025	4	0.001432099
Na^+	8.2	23	0.000356522	1	0.000356522
K^-	1.4	39.1	3.58056E-05	1	3.58056E-05
Fe^{2+}	0.03	55.8	5.37634E-07	4	2.15054E-06
SiO_2	2.1	60.1	3.49418E-05	0	0

I = 0.004682069

I increases with increasing concentrations of ions, so the concentration of ion in B is higher then A

Q3 Calculate the activity coefficient (γ) of Mg^{2+} in an aqueous solution have I = 5×10^{-2} at 15°C if A = 0.5000, B = 0.3262, a = 8, & $-log^{\gamma} = \frac{Az^2I^{1/2}}{1+aBI^{1/2}}$

$$\gamma = 10^{-\left(\frac{0.5x4x0.224}{1+8x0.3262x0.224}\right)} = 10^{-0.283}$$

$$\gamma = 0.52$$

Q4 Calculate the ionic strength (m are in ppm)

Ca^{2+}	Mg^{2+}	Na^+	HCO_3^-	SO_4^{-2}	Cl^-	pH
93.9	22.9	19.1	344	85.0	9.0	7.20

Using excel sheet

	ppm	Mw	m	ζ^2	$m\times\zeta^2$
Ca^{2+}	93.9	40.1	0.002341646	4	0.009366584
Mg^{2+}	22.9	24.3	0.000942387	4	0.003769547
Na^+	19.1	23	0.000830435	1	0.000830435
HCO_3^-	344	61	0.005639344	1	0.005639344
SO_4^{-2}	85	96.1	0.000884495	4	0.003537981
Cl^-	9	35.5	0.000253521	1	0.000253521
H+			6.30957E-08	1	6.30957E-08

I = 0.011698738

Q8 using previous question, Calculate the $SI_{calcite}$ if $[CO_3^{-2}] = 3.4\times10^{-5}$, & What does SI indicate ($a = 5\times10^{-8}$, $Ksp = 4.27\times10^{-8}$, A = 0.5085, B = 3281×10^4, equation in Q3)

$CaCO_{3(s)} \Leftrightarrow Ca^{2+}_{(aq)} + CO_3^{2-}{}_{(aq)}$

From Q3: $(Ca^{2+}) = 2.34\times10^{-3}$ & γ (as Q6)=0.650

$[Ca^{2+}] = 2.34\times10^{-3}\times0.65 = 1.52\times10^{-3}$

$[CO_3^{-2}] = 3.4\times10^{-5}$

$IAP = [Ca^{2+}][CO_3^{2-}] = 1.52\times10^{-3} \times 3.4\times10^{-5} = 5.17\times10^{-8}$

SI = log(IAP/Ksp) = 0.079

SI > 0 (& also IAP > Ksp), This mean that the solution is supersaturated with respect to calcite & so calcite precipitate according to the following reaction:

$CO_3^{2-}{}_{(aq)} + Ca^{2+}_{(aq)} \rightarrow CaCO_{3(s)}$

STRATEGIES

(General Chemistry, 7Ed, Ch17: Solubility & Simultaneous)

CALCULATING OF Ksp & SOLUBILITY

Strategy

$A_{(s)}$	⇔	$bB_{(aq)}$	+	$cC_{(aq)}$
		bX		cX

$Ksp = [aX]^a[bX]^b$ At equilibrium

$IAP = [aX]^a[bX]^b$ At any time

At 25 °C, the solubility of AgCl = 1.34×10^{-5}M. Calculate the solubility product (Ksp) for AgCl

AgCl	⇔	Ag^+	+	Cl^-
1mol		1mol		1mol
X		X		X

$X = 1.34\times10^{-5}$ mol/L

$Ksp = X^2 = 1.80\times10^{-8}$

The solubility of a salt A_2B is found to be 3.0×10^{-4} M. What is the value of Ksp?

A_2B	⇔	2A	+	B
X		2X		X
3×10^{-4}		6×10^{-4}		3×10^{-4}

$Ksp = (6\times10^{-4})^2\times(3\times10^{-4}) = 1.08\times10^{-10}$

The solubility of calcium fluoride CaF_2 in pure water is 2.15×10^{-4}M. What is the value of Ksp?

CaF_2	⇔	Ca^{2+}	+	$2F^-$
1mol		1mol		1mol
2.15×10^{-4}		2.15×10^{-4}		4.3×10^{-4}

$Ksp = (2.15\times10^{-4})\times(4.3\times10^{-4})^2 = 4.0\times10\text{-}11$

What is the molar solubility of CuI in water? Determine $[Cu^+]$ & $[I^-]$ at equilibrium if $Ksp=1.3\times10^{-12}$

CuI	⇔	Cu^+	+	I^-
X		X		X

$Ksp = X^2 = 1.3\times10^{-12}$

X = 1.1x10-6

Calculate the solubility for BaC_2O_4 ($Ksp = 1.2\times10^{-7}$)

BaC_2O_4	⇔	Ba^{2+}	+	$C_2O_4^{2-}$
X		X		X

$Ksp = X^2 = 1.2\times10^{-7}$

$X = 3.5\times10^{-4}$

Calculate the solubility for Ag_3PO_4 ($Ksp= 1.8\times10^{-18}$)

Ag_3PO_4	⇔	$3Ag^+$	+	PO_4^{3-}
X		3X		X

$Ksp = 27X^4 = 1.8\times10^{-18}$

$X = 1.61\times10^{-5}$

Calculate the solubility (in g/l) of CaF_2 in water at 25 °C, if $Ksp= 3.4\times10^{-11}$, Mw of CaF_2 = 78 g/mole

CaF_2	⇔	Ca^{2+}	+	$2F^-$
1mol		1mol		2mol
X		X		2X

$Ksp = 4X^3 = 3.4\times10^{-11}$

$X = 2.0\times10^{-4}$mol/L

S = 0.016g/L

Calculate the solubility of $Ca_3(PO_4)_2$ in water if the solubility product is 1.08×10^{-23}

$Ca_3(PO_4)_2$	⇔	$3Ca^{2+}$	+	$2PO_4^{3-}$
1mol		3mol		2mol
X		3X		2X

$Ksp = (3X)^3(2X)^2 = 108X^5 = 1.08\times10^{-23}$

$X = 10^{-5}$mol/L

What is the solubility of $PbCl_2$ in grams per 100.0 mL at 25°C? $Ksp= 1.7\times10^{-4}$, Mw of $PbCl_2$ = 278.11 g/mol

$PbCl_2$	⇔	Pb^{2+}	+	$2Cl^-$
1mol		1mol		2mol
X		X		2X

$Ksp = (X)(2X)^2 = 4X^3 = 1.7\times10^{-4}$

X = 0.035mol/L

S = 9.71g/L = 0.97g/100L

The solubility of calcium sulfate ($CaSO_4$) is 0.67g/L calculate the Ksp if Mw of $CaSO_4$ is 163.2g/mol

$CaSO_4$	⇔	Ca^{2+}	+	SO_4^{2-}
1mol		1mol		1mol
X		X		X

M = S/Mw = 0.67/163.2 = 4.1×10^{-3}

$Ksp = X^2 = 1.7\times10^{-5}$

Calculate the solubility of copper hydroxide $Cu(OH)_2$ in g/L if the Ksp is 2.2×10^{-22}

$Cu(OH)_2$	⇔	Cu^{2+}	+	$2OH^-$
1mol		1mol		1mol
X		X		2X

$Ksp = 4X^3 = 2.2\times10^{-22}$

$X = 3.8\times10^{-8}$

DETERMINING SOLUBILITY USING Ksp

Solubility are directly proportional to the Ksp
In the comparing of salts with same number of ions, the more the Ksp the more the solubility, but if the number of ions in the salt are different you should be calculating the solubility (*mostly* the higher content of ions the more the solubility)

Which of the following are more soluble?

- AgI (K_{sp} $10^{-16.1}$), CuI (K_{sp} $10^{-11.9}$), or $CaSO_4$ (K_{sp} $10^{-4.3}$)
- Bi_2S_3 (K_{sp} 10^{-73}), Ag_2S (K_{sp} 10^{-50}), CuS (K_{sp} 10^{-56})

AgI, CuI, & $CaSO_4$ all have the same number of ions (2)
So. $CaSO_4$ > CuI > AgI
Bi_2S_3 (5 ions), Ag_2S (3 ions), CuS (2 ions)
Bi_2S_3 > Ag_2S > CuS (you need to calculate the solubility to make sure about result, solubility 10^{-15},10^{-17}, $10^{-28.1}$ "respectively")

COMMON ION EFFECT CALCULATIONS

AB ⇔ A + B, CB ⇔ C + B
Common ion is B

$$[B] = \frac{Ksp1}{[A]} = \frac{Ksp2}{[C]} \; At\ equilibrium$$

$$then: \frac{[A]}{[B]} = \frac{Ksp1}{Ksp2} = L$$

Ratio = L → reaction at equilibrium
Ratio > L → compound contain [A] precipitate
Ratio < L → compound contain [A] dissolved
Concretion of a common ion = concentration of salt (calculate from original solution), & the concentration of another ion = concentration of salt added to solution (from additional salt)

The molar solubility of PbF_2 in 0.10 M $Pb(NO_3)_2$ solution is 2.85 ×10^{-4}M. Calculate Ksp for PbF_2?

$Pb(NO_3)_2$	⇔	Pb^{2+}	+	$2NO_3^-$	$[Pb(NO_3)_2] = [Pb^{2+}] = 0.10M$
		X		2X	تركيز الايون المشترك من المحلول
PbF_2	⇔	Pb^{2+}	+	$2F^-$	$[F^-] = 2x2.85\times10^{-4} = 5.7x10^{-4}$
X		X		2X	تركيز الايون الاخر من الملح المضاف

at equliperum Ksp = $[Pb^{2+}][F^-]^2 = 3.25x10^{-8}$

What is the solubility of PbI_2 in 0.20M NaI? (Ksp= $9.8x10^{-9}$)

NaI	⇔	Na^{2+}	+	I^-	$[NaI] = [I^-] = 0.20M$
PbI_2	⇔	Pb^{2+}		$2I^-$	Ksp = X x $(0.20)^2$
X		X		2X	→ X = $2.45x10^{-7}$

calculate solubility of Ag_2CrO_4 in the following (Ksp = $1.1x10^{-12}$)

- pure water?

Ag_2CrO_4	⇔	$2Ag^+$	+	CrO_4^{2-}	Ksp = $4X^3 = 1.1x10^{-12}$
X		2X		X	X = $6.5x10^{-5}$

- 0.10M $AgNO_3$?

$AgNO_3$	⇔	Ag^+	+	NO_3^-	$[AgNO_3] = [Ag^+] =$
X		X		X	0.10M
Ag_2CrO_4	⇔	$2Ag^+$	+	CrO_4^{2-}	Ksp = $(0.10)^2(X)$
X		0.10		X	X = $1.1x10^{-10}$

- 0.10M Na_2CrO_4?

Na_2CrO_4	⇔	$2Na^+$		CrO_4^-	$[AgNO_3] = [Ag^+] =$
X		X		X	0.10M
Ag_2CrO_4	⇔	$2Ag^+$	+	CrO_4^{2-}	Ksp = $(0.10)(2X)^2$
X		2X		0.10	X = $1.66x10^{-6}$

adding CrO_4^- increase the solubility of Ag_2CrO_4 more than Ag^+, & the solubility of Ag_2CrO_4 are higher in the pure water (good example of the common ion effect)

PREDICTING IF PRECIPITATE WILL FORM

1st. Calculate the concentrations in mixture
2nd. Calculate IAP, & Compare IAP & Ksp

	IAP vs Ksp	SI	
supersaturation	IAP > Ksp	+ve	precipitation
Saturation	IAP = Ksp	0	Equilibrium
Undersaturation	IAP < Ksp	-ve	Dissolution

$$SI = log^{\frac{IAP}{Ksp}}$$

If 2.00mL of 0.200M NaOH are added to 1.00 L of 0.100 $CaCl_2$, $Ca(OH)_2$ will precipitate? Ksp for $Ca(OH)_2$ $8x10^{-6}$

NaOH	⇔	Na^+	+	OH^-	
$4x10^{-4}$				$4x10^{-4}$	IAP = 0.1 x $(4x10^{-4})^2$
$CaCl_2$	⇔	Ca^{2+}	+	$2Cl^-$	IAP = $1.6x10^{-8}$
0.100		0.100			IAP < Ksp
$Ca(OH)_2$	⇔	Ca^{2+}		$2OH^-$	$Ca(OH)_2$ will dissolved
		0.100		$4x10^{-4}$	into ions

Will a precipitate of PbI_2 form? 100.0mL of 0.0500M $Pb(NO_3)_2$ mixed with 200.0 mL of 0.100M NaI? (Ksp PbI_2 = $9.8x10^{-9}$)

$Pb(NO_3)_2$	⇔	Pb^{2+}	+	$2NO_3^-$	
$5x10^{-3}$mol		$5x10^{-3}$mol			IAP =$5x10^{-3}(0.02)^2$
NaI	⇔	Na^{2+}	+	I^-	= $2x10^{-6}$
0.02mol				0.02mol	IAP > Ksp
PbI_2	⇔	Pb^{2+}		$2I^-$	PbI_2 will
		$5x10^{-3}$		0.02	precipitate

Suppose you mix 100.0 mL of 0.200M $BaCl_2$ with 50.0 mL of 0.0300 Na_2SO_4. $BaSO_4$ precipitate? (Ksp of $BaSO_4$ is $1.1x10^{-10}$)

$BaCl_2$	⇔	Ba^{2+}	+	$2Cl^-$	IAP = 0.020x0.015 = $3x10^{-4}$
0.020		0.020			→ IAP > Ksp
Na_2SO_4	⇔	$2Na^+$	+	SO_4^{2-}	$BaSO_4$ will precipitate
0.015				0.015	according to the following
$BaSO_4$	⇔	Ba^{2+}		SO_4^{2-}	equation
		0.020		0.015	$Ba^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)} \rightarrow BaSO_{4(s)}$

Will a precipitate of $BaSO_4$ form if 50.0mL of 1.0M $Ba(OH)_2$ is mixed with 86.4mL of 0.494M H_2SO_4, Ksp= $1.1x10^{-10}$

$Ba(OH)_2$	⇔	Ba^{2+}	+	$2OH^-$	
1mol		1mol			$[Ba(OH)_2]$ = MV =
0.050		0.050			$50.0x10^{-3}$L x 1.0mol/L =
H_2SO_4	⇔	$2H^+$	+	SO_4^{2-}	0.050mol
1mol				1mol	$[H_2SO_4]$ = MV = $86.4x10^{-3}$L x
0.043				0.043	0.494mol/L = 0.043mol
$BaSO_4$	⇔	Ba^{2+}		SO_4^{2-}	IAP = 0.050 x 0.043 =
		0.050		0.043	$2.15x10^{-3}$ → IAP > Ksp,
					$BaSO_4$ precipitate

ANOTHER EQUATIO

$$\Sigma([x] \times |charge|)p = \Sigma([x] \times |charge|)r$$

$$(A) = \frac{Ksp1}{\gamma[B]}, (C) = \frac{Ksp2}{\gamma[B]}$$

$$I = \frac{1}{2}\Sigma Mz^2 = \frac{1}{2}\Sigma mz^2$$

$$ppm = mg = \frac{mol}{Mwx1000}$$

If I < $5x10^{-3}$: $-log^{\gamma} = Az^2 I^{1/2}, \gamma = 10^{-Az^2 I^{1/2}}$

If I < 0.1 : $-log^{\gamma} = \frac{Az^2 I^{1/2}}{1+aBI^{1/2}}, \gamma = 10^{-\left(\frac{Az^2 I^{1/2}}{1+aBI^{1/2}}\right)}$

If I = 0.5 : $-log^{\gamma} = Az^2\left[\frac{I^{1/2}}{1+I^2} - 0.2I\right]$

Increase in Solubility = $\frac{(x)-[x]}{[x]}$

Chapter Seven
Thermodynamics

- The observation of the transformation of mechanical energy into heat lead to development of thermodynamics science
- Joule demonstrated that expenditure of amount of work always produced the same amount of heat
- **Principle of conservation of energy**: when work is done, heat energy is consumed
- Thermodynamic deal with physical & chemical changes of matter due to work & heat flow (thermo = heat; dynamics = movement)
- Real rocks are end products of long complex processes, that cannot exactly be duplicated in the lab, but we can use thermodynamic measurements & reasoning to investigate nature of these processes

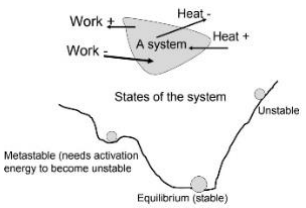
THERMODYNAMICS & SYSTEMS

- Thermodynamics describes the world in terms of certain measurable properties of matter such as volume, P, T, & X (composition)
- **System**: any part of the universe under consideration, & The rest is the surrounding

System	Transfer Energy	Transfer Matter
Open	✔	✔
Closed	✔	✘
Isolated	✘	✘
Variables of a systems		
Intensive variables	**Amounts of materials Independent** P, T, ρ, potential, activity, fugacity	
Extensive variables	**Depend on the amount of material** volume, mass, energy,composition	
Composition of a system is expressed in the following		
Phase	**Homogenous part of a system** physically distinct & separable mechanically. It can be solid, liquid, or gas. (e.g. quartz crystal)	
Component	**Chemical constituent, described of phase composition** (SiO_2 oxide)	

- The number of components, phases, & degrees of freedom are related by the **Gibbs Phase Rule**

(Degree of freedom) F = C – P + 2(P,T)



	q (heat)	W (work)
system → surrounding	-Ve	+Ve
surrounding → system	+Ve	-Ve

LAWS OF THERMODYNAMICS

- **0th Law**: 2 bodies are in thermal equilibrium have the same T, & any 2 bodies in thermal equilibrium with a third body are themselves in equilibrium
- **1st law**: In reversible reaction $\Delta E = q - w$

  dE = dq – dw (in small incremental changes)

  ΔE: The increase in internal energy of a system

  q: heat flows ***from*** *the surrounding*, **–w**: work *done* ***by*** *the system*
- The most common form of work that can be done by a system is to expand against a constant pressure

  $$\Delta E = \Delta q - p\Delta V$$

  dE = dq – dp × dv (in small incremental changes)

- ***Enthalpy (ΔH) :*** function of state of the system

  $$\Delta H = E + PV = q - PV$$
- ΔH at constant P is equal to heat absorbed by the system during that change (**ΔH = Δq**)
- Enthalpy values for elements & compounds are defined at STP (for any Element = 0 such as O_2, N...)
- **Enthalpy of formation (H^0_f)**: heat absorbed or given off by chemical reactions in the compounds, ions, & molecules form from elements in the standard state
- **Heats of Reaction (H^0_R) in Kcal/mol**

  $$\Delta H^\circ_R = \Sigma \Delta H^\circ_{f_{product}} - \Sigma \Delta H^\circ_{f_{reactant}}$$
- **Calorie**: the amount of heat required to raise the T of a 1g of water from 14.5 to 15.5°C

Example

$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(g)}$

ΔH^0_f 0 0 -57.8Kcal

$\Delta H^0_R = 2(-57.80) - 0 = -115.6$ Kcal,Exothermic

$H_2O_{(l)} \rightarrow 2H_2O_{(g)}$

H^0_f -68.32 -57.8Kcal

$H^0_R = -57.80 - -68.32 = +10.25$ Kcal, Endothermic

- When heat is added to a solid, liquid, or a gas T increases. This observation can be stated as:

  $$\Delta q = C\Delta T$$

  q: heat added, **T:** T in Kelvin, **C:** A heat capacity

  $$C = a + (b \times 10^{-3})T + (c \times 10^{-6})T^2$$

  a, b, c: constants derived by fitting an algebraic equation to experimentally determined data in coordinates of C & T

  $$\Delta H - \Delta H_{\circ} = a(T - T_{\circ}) + \frac{b \times 10^{-3}}{2}[T^2 - T_{\circ}^2] + \frac{c \times 10^{-6}}{3}[T^3 - T_{\circ}^3]$$
- **2nd law:** In reversible reaction

  $$dS = \frac{dq}{T} \text{ or } \Delta S = \frac{\Delta q}{T}$$

  dS: entropy of a system, **dq**: heat, **T**:absolute temperature

Reaction	Spontaneous	ΔS
Reverseable	No	dS = dq/T
Irreversible	Yes	dS > dq/T

  - Efficiency of steam engines lead to the development of the concept of **Entropy**
  - A certain amount of enthalpy (heat) is converted to entropy (S). not to work
- **3rd law:** The heat capacities of pure crystalline substances become 0 at absolute 0**: dS =0**

  $$_0\int^T dS = C_0\int^T dT/T$$

  $$\Delta S^0_R = \Sigma n S^0_{f\ Products} - \Sigma n S^0_{f\ Reactants}$$

$H_2O_{(l)} \rightarrow 2H_2O_{(g)}$

S^0_f 16.71cal/° 45.10cal/°

S^0_f = 45.10 - 16.71 = +23.39 cal/°

Vapor molecules are more randomly distributed

THE GIBBS FREE ENERGY

- The increase ΔH in reversible reaction is lowered because certain amount of H consumed by S

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G^\circ_R = \Delta H^\circ_R - T\Delta S^\circ_R = \Sigma n\Delta G^\circ_{product} - \Sigma n\Delta G^\circ_{reactant}$$

- The standard Gibbs free energy of formation of a compound (G°_f) is the change in the free energy of the reaction by which it forms from the elements

Reaction	q (heat)	w	ΔH	ΔG	equ. Direction
Endothermic	+ve (absorb)	-	+	-	→
Exothermic	-ve (release)	+	-	+	←
Equliperum	0 (no rxn)	0	0	0	↔

$$\Delta G = \Delta G^\circ + RTln^K$$

$$at\ equilibrium\ \Delta G = 0, then: \Delta G^\circ = -RTln^K$$

$$K = 10^{-\left(\frac{\Delta G^\circ}{1.364}\right)}\ in\ cal, K = 10^{-\left(\frac{\Delta G^\circ}{5.709}\right)}\ in\ Jol$$

- **Van't Hoff Equation:** to calculate K at other T

$$ln^K - ln^{K^\circ} = \left(\frac{-\Delta H^\circ}{R}\right)\left(\frac{1}{T} - \frac{1}{T^\circ}\right)$$

$$log^K - log^{K^\circ} = \left(\frac{-\Delta H^\circ}{2.3025R}\right)\left(\frac{1}{T} - \frac{1}{298.15}\right)$$

R = 1.987 cal/mol°K

EXAMPLE calculate the solubility of amorphous silica between 0° – 100°C, which reacts with water to form silicic acid according to the following equation

$SiO_2 + 2H_2O \Leftrightarrow H_4SiO_4$

$\Delta G^\circ_R = \Sigma n\Delta G^\circ_{product} - \Sigma n\Delta G^\circ_{reactant}$ = 4.044 kcal

$K^\circ = 10^{-\Delta G^\circ R/1.36} = 10^{-2.96}$

$\Delta H^0_R = \Sigma nH^0_{f\ Products} - \Sigma nH^0_{f\ Reactants}$ = +3.47 kcal

the reaction is endothermic, so K increase with T

$$log^K - -2.96 = \left(\frac{3.47x10^3}{2.3025x1.987}\right)\left(\frac{1}{T} - \frac{1}{298.15}\right)$$

At T =273 = 0.00366 → $K_{0°C} = 10^{-3.2}$

At T =373 = 0.00268 → $K_{100°C} = 10^{-2.45}$

solubility at 100°C is higher (S increases with T)

EXAMPLE calculate ΔH, ΔS & ΔG when fluorite (CaF_2) dissolves in water in the standard state. Use the results to calculate the K at STP

	CaF_2 ⇔	Ca^{2+} +	$2F^-$
H^0_f	- 1219.6	-542.8 kJ/mol	-323.6 kJ/mol
S^0_f	68.9	-53.1 J/mol°C	-26.6 J/mol/deg
G°_f	-1167.3	-553.6 kJ/mol	-278.8 kJ/mol

ΔH^0_R = + 11.6 kJ/mol

ΔS^0_R = -149.6 J/mol/deg

ΔG = ΔH – TΔS

ΔG^0_R =+56.1 kJ/mol

$LogK = 10^{-G/5.709}$ → K=1.58x10^{-10}

(ΔG can be calculated using ΔG^0_f values from tables of ΔG^0_f (such as ΔH° & ΔS°)

Le Chatelier's rules (from chemistry 102,ch17)		
Changes	Shift of Equilibrium	
Increase Concentration of product	Toward Reactants	←
Increase Concentration of reactant	Toward product	→
Increase pressure (decrease volume)	Toward a fewer moles of gasses	
Increase temperature (of endothermic reactions)	Toward product	→
Increase temperature of (of exothermic reactions)	Toward reactant	←

CHEMICAL WEATHERING

- Types of chemical weathering:
  I. **Congruent**: formed by ions without another compound (e.g. Calcite dissolution)
  II. **Incongruent**: formed by another compounds as well as ions & molecules (e.g. Al-silicates)
- **All chemical weathering are redox reactions**
- **The products of weathering include:** new minerals, ions & molecule, & Unreactive grains (zircon, quartz)

(1) K-feldspar ⇔ kaolinite

$2KAlSi_3O_8 + 9H_2O + 2H \Leftrightarrow Al_2Si_2O_5(OH)_4 + 2K^+ + 4H_4SiO_4$

$\Delta G^0_R = \Sigma nG^0_{f\ Products} - \Sigma nG^0_{f\ Reactants}$ = +7.103 kcal

$K = [H_4SiO_4]^4[K^+]^2/[H^+]^2 = 10^{-(7.103/1.364)} = 10^{-5.21}$

$4\log[H_4SiO_4] + 2\log[K^+] - 2\log[H^+] = -5.21$

$\log[K^+]/[H^+] = -2\ \log[H_4SiO_4] + (-2.61)$

(2) Kaolinite ⇔ Gibbsite

$Al_2Si_2O_5(OH)_{4(s)} + 5H_2O_{(l)} \Leftrightarrow 2Al(OH)_{3(s)} + 2H_4SiO_{4(aq)}$

ΔG^0_R = +12.76 kcal → $K = 10^{-4.68}$

$\log[H_4SiO_4] = -4.68$

(3) Microcline ⇔ Muscovite

$KAlSi_3O_{8(s)} + 12H_2O_{(l)} + 2H^+_{(aq)} \Leftrightarrow KAl_3Si_3O_{12}(OH)_{2(s)} + 2K^+_{(aq)} + 6H_4SiO_{4(aq)}$

ΔG^0_R = +16.184kcal → $K = 10^{-5.93}$

$\log[K^+]/[H^+] = -3\ \log[H_4SiO_4] - 5.93$

(4) Muscovite ⇔ Kaolinite

$KAl_3Si_3O_{12}(OH)_{2(s)} + 3H_2O_{(l)} + 2H^+_{(aq)} \Leftrightarrow + 2K^+_{(aq)} + Al_2Si_2O_5(OH)_{4(s)}$

ΔG^0_R = - 11.059kcal → $K = 10^{-4.05}$

$\log[K^+]/[H^+]$ = + 4.05

$\log[K^+]/[H^+]$ = 4.05

(5) Muscovite ⇔ Gibbsite

$KAl_3Si_3O_{12}(OH)_{2(s)} + 9H_2O_{(l)} + H^+_{(aq)} \Leftrightarrow 2Al(OH)_{3(s)} + K^+_{(aq)} + 3H_4SiO_{4(aq)}$

ΔG^0_R = +13.603kcal → $K = 10^{-9.97}$

$\log[K^+]/[H^+] = -3\log[H_4SiO_4] - 9.97$

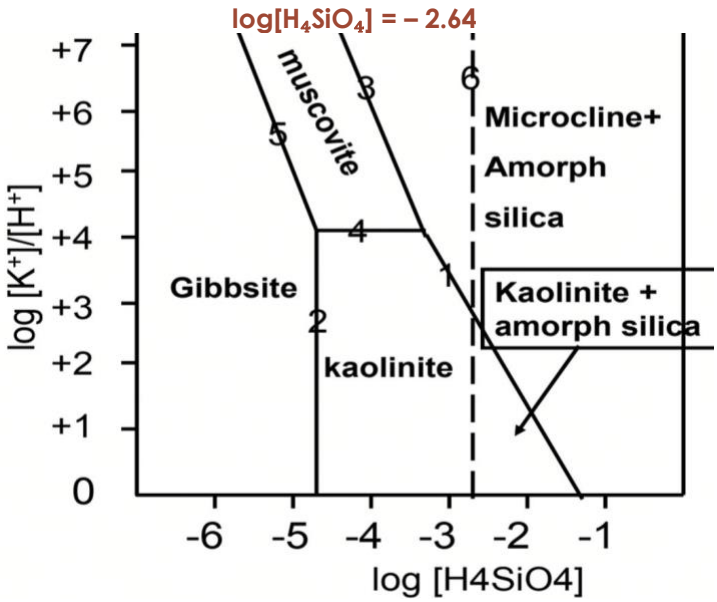
$\log[K^+]/[H^+] = -3\ \log[H_4SiO_4] - 9.97$

(6) Amorphous Silica ⇔ Silicic Acid

$SiO_{2(s)} + 2H_2O_{(l)} \Leftrightarrow H_4SiO_{4(aq)}$

ΔG^0_R = +3.604kcal → $K = 10^{-2.64}$

$\log[H_4SiO_4] = -2.64$



PROBLEMS

Q1 Calculate the enthalpy change & the standard free energy change when fluorite (CaF_2) dissolves in water in the standard state

- ΔH_f°: $CaF_{2(s)}$ =-291.5, $Ca^{2+}_{(aq)}$ =-129.74, $F^-_{(aq)}$ =-79.5
- ΔG_f°: $CaF_{2(s)}$ =-279.0, $Ca^{2+}_{(aq)}$ =-132.3, $F^-_{(aq)}$ = - 132.8

$$CaF_{2(s)} \leftrightarrow Ca^{2+}_{(aq)} + 2F^-_{(aq)}$$

$$\Delta H_R^\circ = (-159 - 129.74) - (-291.5) = +2.76Kcal$$
$$\Delta G_R^\circ = (-132.3 - 132.8) - (-279.0) = +13.9Kcal$$

Q2 Based on the result in Q1, predict how the solubility of fluorite varies with temperature

+ve ΔH_R° (endothermic, Absorb heat): as T increases the position of equilibrium will *shift toward the products* (the solubility of reactant increase) to reach new equliperum state at new T (according to *Le Chatelier's rules*)

Q3 Calculate the solubility of fluorite in water at 10, 20, & 30°C & express each in terms of the concentration of Ca^{2+} in mg/L. (Assume γ = 1, Mw $_{Ca2+}$ = 40.08g/mol, R = 1.987cal/molK, T. = 279.15°K)

$$CaF_{2(s)} \leftrightarrow Ca^{2+}_{(aq)} + 2F^-_{(aq)}$$

$$K^\circ = 10^{-\left(\frac{\Delta G^\circ}{RT^\circ}\right)} = 10^{-\left(\frac{13.9}{1.364}\right)} = 6.45x10^{-11}$$
$$\Delta H_R^\circ = +2.76Kcal = 2.76x10^3 cal$$
$$K_{10^\circ} = e^{ln^{6.45x10^{-11}} - \left(\frac{2760}{1.987}\right)\left(\frac{1}{283.15} - \frac{1}{298.15}\right)} = 10^{-10.3}$$
$$K_{20^\circ} = 10^{\left[log^{6.45} - 11 - \left(\frac{2760}{4.575}\right)\left(\frac{1}{293.15_x} - \frac{1}{298.15}\right)\right]} = 10^{-10.22}$$
$$K_{30^\circ} = 10^{\left[log^{6.45} - 11 - \left(\frac{2760}{4.575}\right)\left(\frac{1}{303.15_x} - \frac{1}{298.15}\right)\right]} = 10^{-10.16}$$
$$(\gamma = 1) \rightarrow K_x = (X)(2X)^2 = [X][2X]^2 = 4X^3$$
$$[Ca^{2+}]_{10^\circ} = \left(\frac{10^{-10.30}}{4}\right)^{\frac{1}{3}} x\, 40.08\, x\, 1000 = 9.31mg/L$$
$$[Ca^{2+}]_{20^\circ} = \left(\frac{10^{-10.22}}{4}\right)^{\frac{1}{3}} x\, 40.08\, x\, 1000 = 9.90mg/L$$
$$[Ca^{2+}]_{30^\circ} = \left(\frac{10^{-10.16}}{4}\right)^{\frac{1}{3}} x\, 40.08\, x\, 1000 = 10.4mg/L$$

Q4 Calculate K° for the reaction of albite ($NaAlSi_3O_8$) to form kaolinite, & write the linear equation

	n [mol]	ΔG_f° [Kcal/mol]
$NaAlSi_3O_8$	2	-884.8
H_2O	9	-56.687
H^+	2	0
$Al_2Si_2O_5(OH)_4$	1	-906.84
H_4SiO_4	4	-312.66
Na^+	2	-62.593

$$2NaAlSi_3O_{8(s)} + 9H_2O_{(l)} + 2H^+_{(aq)} \Leftrightarrow Al_2Si_2O_5(OH)_{4(s)} + 4H_4SiO_{4(aq)} + 2Na^+_{(aq)}$$
$$\Delta G_R^\circ = \Sigma n \Delta G^\circ_{f_{product}} - \Sigma n \Delta G^\circ_{f_{reactint}} = -2883cal$$
$$K = e^{\frac{-\Delta G^\circ}{RT}} = 130.32 = \frac{[H_4SiO_4]^4[Na^+]^2}{[H^+]^2}$$
$$log\frac{[H_4SiO_4]^4[Na^+]^2}{[H^+]^2} = log^{130.32}$$
$$log\frac{[Na^+]}{[H^+]} = -2log^{[H_4SiO_4]} + 1.06$$

The equation of linear (with -ve slope & intersect with Y-axis at point 1.06)

Q5 using the following table, calculate log[Na^+]/[H^+] & log [H_4SiO_4], if (A for γ is: Na^+ = 4.25, H^+ = 9, & H_4SiO_4 = 0)

Ions	ppm	Ions	ppm
HCO_3^-	101	Mg^{2+}	7.6
SO_4^{2-}	41	Na^+	11
Cl^-	15	K^+	3.1
NO_3^-	1.9	SiO_2	5.9
Ca^{2+}	34	pH = 7.2	

1st step: change ppm (mg/L) into mol/L

Ions	ppm [mg/L]	Mw [g/mol]	Concentrations [mol/L]
HCO_3^-	101	61.0	$1.66x10^{-3}$
SO_4^{2-}	41	96.1	$3.27x10^{-4}$
Cl^-	15	35.5	$4.23x10^{-4}$
NO_3^-	1.9	62.0	$3.06x10^{-5}$
Ca^{2+}	34	40.1	$8.48x10^{-4}$
Mg^{2+}	7.6	24.3	$3.13x10^{-4}$
Na^+	11	23.0	$4.78x10^{-4}$
K^+	3.1	39.1	$7.93x10^{-5}$
SiO_2	5.9	60.1	$9.82x10^{-5}$
H^+			$10^{-7.2}$

2nd step: Calculate the activity coefficient (γ)

$I = ½\Sigma mz^2 = 4.4x10^{-3} \rightarrow I < 5x10^{-3}$

For [Na^+]: $\gamma = 10^{-Az^2I^{½}} = 10^{-4.25x(4.4x10^{-3})^{½}} = 0.523$

For [H^+]: $\gamma = 10^{-Az^2I^{½}} = 10^{-9x(4.4x10^{-3})^{½}} = 0.253$

For [H_4SiO_4]: $\gamma = 10^{-Az^2I^{½}} = 10^{-0x(4.4x10^{-3})} = 1$

3rd step: Calculate the activity

Activity = $0.523x4.78x10^{-4} = 2.50x10^{-4}$

Activity = $0.253x6.311x10^{-8} = 1.60x10^{-8}$

$H_4SiO_4 \rightarrow SiO_2 + 2H_2O$, n SiO_2 = n H_4SiO_4

Concentration H_4SiO_4 = Activity = $9.82x10^{-5}$

4th step: Calculate the logarithms

$$log_{10}\frac{[Na^+]}{[H^+]} = log_{10}\frac{2.5x10^{-4}}{1.6x10^{-8}} = log_{10}^{7951} = 4.19$$
$$log_{10}[H_4SiO_4] = log_{10}^{9.82x10^{-5}} = log_{10}^{7951} = -4.01$$

Q6 Calculate the value of ΔG^0_R for BaF_2 given that the concentration of Ba^{2+} in a saturated solution = $1.12x10^{-2}$m/L, & have an ionic strength of 0.01 (R = 1.987cal/molK & T. = 298.15°K)

$BaF_{2(s)}$	→	$Ba^{2+}_{(aq)}$	+	$2F^-_{(aq)}$
1mol		1mol		2mol
$1.12x10^{-2}$m/L		$1.12x10^{-2}$m/L		$2.24x10^{-2}$m/L

$$\gamma_{Ba} = 10^{-\left(\frac{0.5085x4x0.01^{½}}{1+5x0.3281xI^{½}}\right)} = 0.17$$
$$\gamma_F = 10^{-\left(\frac{0.5085x0.01^{½}}{1+3.5x0.3281x0.01^{½}}\right)} = 0.046$$

[Ba]=$1.7x1.12x10^{-3}=1.9x10^{-3}$

[Fe]=$4.6x2.24x10^{-4}=1.02x10^{-3}$

$$\Delta G = \Delta G^\circ + RTln^K \rightarrow \Delta G^\circ = -RTln^{K^\circ}$$
$$\Delta G^\circ = -592.4ln^{0.0019x0.00102^2}$$
$$\Delta G^\circ = 11873cal/mol$$
$$\Delta G^\circ = 11.873Kcal/mol$$

Chapter Eight
Oxidation-Reduction Reactions (REDOX Reactions)

- **Elements divided into:** Metals & Non-Metal

Metal	Non-metal
Loss e (e donor)	Gain e (e acceptor)
Oxidation	Reduction
Reducing agent	Oxidizing agent
Increase in ON	Decrease in ON

- These are also called **electronegativities**
- **Alkali metals & alkaline earths** are always electron donors regardless of the environment
- **Transition element (Cu, Fe..)** loose variable number of e depending on the environments
- **non-metals (N, C, S..)** take-up variable number of electrons depending on their availability

BALANCING OF REDOX REACTIONS

Elements	V or OS
All elements in pure form (e.g. F,O_2...)	0
H	+1
H in H+(I or II groups), e.g. Li, Na..	-1
O	-2
O in peroxides (O_2H_2, O_2F..)	-1
compound & ions with n charge	n
Compound without charge	0

$V_{compound} = \Sigma n V_{element} = 0 \text{ or } n$

EXAMPLE Calculate the V of iron in FeO, Fe_2O_3

Fe O

X*1 + -2*1 = 0 → X = +2

X = +2

Fe_2 O_3

X*2 + -2*3 = 0 → X = +3

- **Rules For Balancing equations:**
  1. Determine oxidized & reduced agent
  2. Balancing the electron in each half
  3. Balancing the mass in each half
  4. Balancing O by H_2O, & H by H^+

EXAMPLE Balance Fe + Cl_2 → $FeCl_3$

Reaction:	Fe	+	Cl_2	→	$FeCl_3$
Valence :	0		0		+3, - 1
Oxidation	Fe	→	Fe^{3+}	+	$3e^-$
Reduction	Cl_2	+	$2e^-$	→	$2Cl^-$

By multiply the first half by 2 & the other by 3

	2Fe	→	$2Fe^{3+}$	+	$6e^-$
	$3Cl_2$	+	$6e^-$	→	$6Cl^-$
Over all:	2Fe	+	$3Cl_2$	→	$2FeCl_3$

The total exchange of electrons = 6

Elements	O	R
Metals	✔	✘
Non-Metals	✘	✔
Cations	✘	✔
Anions	✔	✘
Complex Anions (NO_3^-,SO_4^{-2})	✘	✔
Complex Cations (NH_4^+)	✔	✘

EXAMPLE Balance $FeS_2 + O_2 \rightarrow Fe(OH)_3 + SO_4^{2-}$

FeS_2	+	O_2	→	$Fe(OH)_3$	+	SO_4^{2-}
+2,-1		0		+3,-2,+1		+6,-2

Fe loss $1e^-$, & S loss $7e^-$, & O gains 2e

Fe^{2+} → Fe^{3+} + e^-

$2S^-$ → $14e^-$ + $2S^{6+}$

$2O$ + $4e^-$ → $2O^{-2}$

by combining the first & second equations

FeS_2 → Fe^{3+} + $15e^-$ + $2S^{6+}$

$2O$ + $4e^-$ → $2O^{-2}$

To Balancing e, multiply FeS_2 by 4, & O_2 by 15

$4FeS_2$ → $4Fe^{3+}$ + $60e^-$ + $8S^{6+}$

$30O$ + $60e^-$ → $30O^{-2}$

by combining this 2 equations

$4FeS_2 + 15O_2 \rightarrow 4Fe(OH)_3 + 8SO_4^{-2}$

O, & H must be Balancing

$4FeS_2 + 15O_2 + 14H_2O \rightarrow 4Fe(OH)_3 + 8SO_4^{-2} + 16H^+$

The weathering of 1mol pyrite releases 4molH+

Thus creating a strongly acidic environment

- Discharge of acidified mine waters in streams & lakes can be harmful to plant & animal life
- Such a reaction takes place in mines (in particular sulphide ores) when pyrite become exposed to oxygenated waters
- Pyrite found in igneous, metamorphic, & shale

THE ELECTROMOTIVE SERIES

- The ability of elements to act as electron donors or acceptors depends on the extent to which their orbitals are filled with electrons
- Thermodynamics helps us to rank elements according to strength as REDOX agents
- Let us consider the reaction:

$$Zn + Fe^{2+} \rightarrow Zn^{2+} + Fe$$

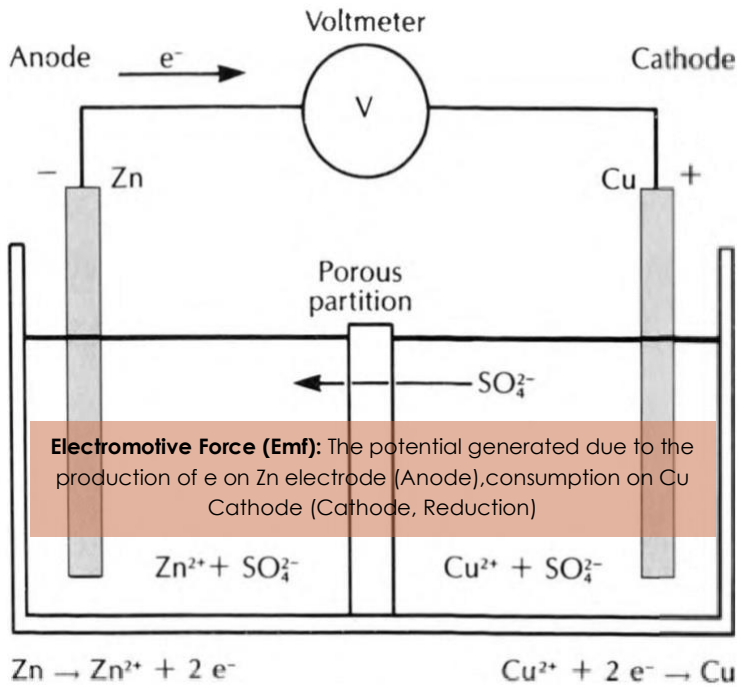
Zn is stronger reducing agent (oxidized), & ***force*** Fe to accepted → **Fe Precipitate & Zn Dissolved**

- Can this reaction proceed to the left?
  $\Delta G^{o}f = (0 - 35.2) - (-18.85 - 0) = -16.29$Kcal
  this reaction can only proceed as written ($-\Delta Gf$)

ΔG	Reaction direction	Type of reaction
- ΔG	→	Endothermic
+ΔG	←	Exothermic
0	↔	Equliperum

Example

$Zn + Fe^{2+} \rightarrow Zn^{2+} + Fe$, $\Delta G^{o} = -16.29$kcal
$Fe + Cu^{2+} \rightarrow Fe^{2+} + Cu$, $\Delta G^{o} = -34.51$kcal
$Cu + 2Ag^{+} \rightarrow 2Ag + Cu^{2+}$, $\Delta G^{o} = -21.21$kcal
As reducing agent: Zn > Fe > Cu > Ag
Zn is the strongest RE & displaces the ions of all metals located below (Electromotive series)



Electromotive Force (Emf): The potential generated due to the production of e on Zn electrode (Anode),consumption on Cu Cathode (Cathode, Reduction)

Electromotive cell		
	Oxidation	Reduction
Agent	Reducing	Oxidizing
Electrode	Anode	Cathode
Electron	Loss electron	Gain electron
Electrode Charge	-ve	+ve
O-Number	Increasing	Decreasing
Formula	$nX \rightarrow X^{n+} + ne$	$X^{n+} + ne \rightarrow nX$
Reducing agent	Stronger	Weaker
potential [V]	Less	More
ΔG°	-ve, endo, →	+ve, exo, ←
Salt ions	Gain –ve ions	Gain +ve ions
[Ions]	Increase	Decrease
Mass	Dissolved	Preceptate

- Addition of the 2 half-cell reactions gives:
  $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$, $\Delta G = -50.8$ kcal

at equilibrium: $K = \frac{[Zn^{2+}]}{[Cu^{2+}]} = 10^{-\left(\frac{\Delta G}{1.364}\right)} = 10^{37.24}$

$\Delta G^{o} = nFE^{o}$, $\Delta G = nFE$

F = Farady constant = 96,489 Co/mole = 23.06 kcal/volt/gram
n = Number of electrons transferred
E = electromotive Force

Stronger reducing agents (oxidation, - ve Anode, loss e⁻)

Reducing agent	Oxidizing agent		Standard electro potential, V
Cs	→ Cs^{+}	$+e^{-}$	−3.03
Li	→ Li^{+}	$+e^{-}$	−3.04
K	→ K^{+}	$+e^{-}$	−2.94
Ba	→ Ba^{2+}	$+2e^{-}$	−2.91
Sr	→ Sr^{2+}	$+2e^{-}$	−2.90
Ca	→ Ca^{2+}	$+2e^{-}$	−2.87
Na	→ Na^{+}	$+e^{-}$	−2.71
Rb	→ Rb^{+}	$+e^{-}$	−2.60
Y	→ Y^{3+}	$+3e^{-}$	−2.40
Mg	→ Mg^{2+}	$+2e^{-}$	−2.36
La	→ La^{3+}	$+3e^{-}$	−2.36
Ce	→ Ce^{3+}	$+3e^{-}$	−2.32
Sc	→ Sc^{3+}	$+3e^{-}$	−2.03
Be	→ Be^{2+}	$+2e^{-}$	−1.97
Th	→ Th^{4+}	$+4e^{-}$	−1.83
Al	→ Al^{3+}	$+3e^{-}$	−1.70
U	→ U^{4+}	$+4e^{-}$	−1.38
Mn	→ Mn^{2+}	$+2e^{-}$	−1.18
Nb	→ Nb^{3+}	$+3e^{-}$	−1.10
V	→ V^{3+}	$+3e^{-}$	−0.87
Zn	→ Zn^{2+}	$+2e^{-}$	−0.76
Cr	→ Cr^{3+}	$+3e^{-}$	−0.74
S^{2-}	→ S	$+2e^{-}$	−0.44
Fe	→ Fe^{2+}	$+2e^{-}$	−0.41
Cd	→ Cd^{2+}	$+2e^{-}$	−0.40
Co	→ Co^{2+}	$+2e^{-}$	−0.28
Ni	→ Ni^{2+}	$+2e^{-}$	−0.24
Mo	→ Mo^{3+}	$+3e^{-}$	−0.20
Sn	→ Sn^{2+}	$+2e^{-}$	−0.14
Pb	→ Pb^{2+}	$+2e^{-}$	−0.13
H_2	→ $2H^{+}$	$+2e^{-}$	0.00
Bi	→ Bi^{3+}	$+3e^{-}$	+0.29
Cu	→ Cu^{2+}	$+2e^{-}$	+0.34
Cu	→ Cu^{+}	$+e^{-}$	+0.52
$2I^{-}$	→ I_2	$+2e^{-}$	+0.53
Se^{2-}	→ Se	$+2e^{-}$	+0.67
Ag	→ Ag^{+}	$+e^{-}$	+0.80
Hg	→ Hg^{2+}	$+e^{-}$	+0.85
Pd	→ Pd^{2+}	$+2e^{-}$	+0.92
$2Br^{-}$	→ Br_2	$+2e^{-}$	+1.08
Pt	→ Pt^{2+}	$+2e^{-}$	+1.19
$2Cl^{-}$	→ Cl_2	$+2e^{-}$	+1.36
Au	→ Au^{+}	$+e^{-}$	+1.69
Pt	→ Pt^{+}	$+e^{-}$	+2.64
$2F^{-}$	→ F_2	$+2e^{-}$	+2.88

Electromotive Force (Emf)
The potential generated due to the production of e^{-} on Zn electrode (Anode, oxidation), & their consumption on Cu electrode (Cathode, Reduction)

If reaction reached equilibrium there are no more e transferred so the reaction stop

- The element ranked according to strengths as reducing agents using ΔG° & the comparing them to a hydrogen half-cell reaction

$H_{2(g)} \rightarrow 2H^+_{(aq)} + 2e^-$, E° = 0.00

G°(H⁺) = G°(e) = 0.00 by convention

$Zn + 2H^+ \rightarrow Zn^{2+} + H_2\uparrow$

ΔG° = -35.14 - 0 = -35.14 kcal (mean Zn > H)

E° = ΔG°/nF = - 0.76vol

$Cu + 2H^+ \rightarrow Cu^{2+} + H_2\uparrow$

ΔG° = +15.66 kcal, E° = +0.34volts (mean Cu<H)

$$E^\circ_{cell} = E^\circ_{reduction} + E^\circ_{oxidation}$$

$E^\circ_{cell} = E^\circ_{reduction} + E^\circ_{oxidation}$ = -0.76 + (-0.34) =-1.1V

Oxidation: $Zn \rightarrow Zn^{2+} + 2e^-$, - 0.76vol

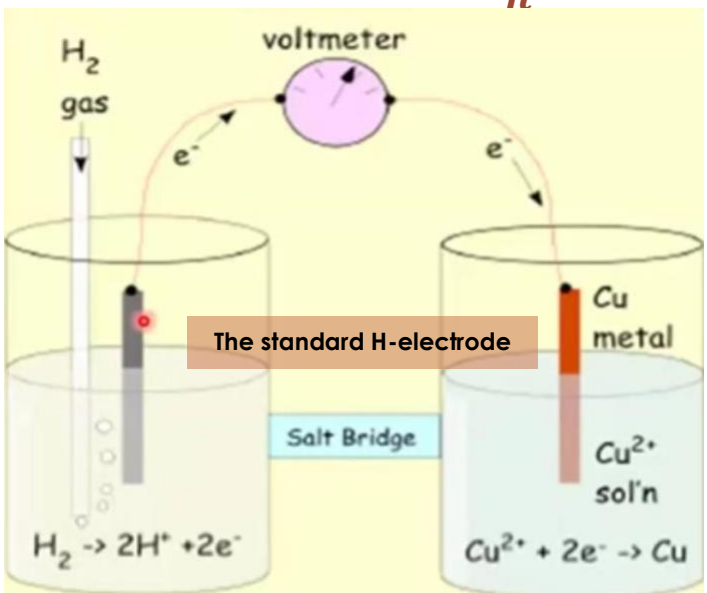
Reduction: $Cu^{2+} + e^- \rightarrow Cu$, - 0.34

- Electromotive series presented in order of decreasing strengths as reducing agents

$$\Delta G = \Delta G^\circ + RT\ln Q = nFE$$

$$E = E^\circ + \frac{2.303RT}{nf}\log^Q = E^\circ + \frac{0.0592\log^Q}{n}$$

$$at\ equilibum: E^\circ = -\frac{0.05916}{n}\log^K$$



EXAMPLE Zn-Cu redox

$E = E^\circ + 0.0592\log([Zn^{2+}]/[Cu^{2+}])/2$

$E = -1.1+0.0296\log([Zn^{2+}]/[Cu^{2+}])$

In the standard state: [X] = 1

E = -1.1+0.0296log(1/1) = - 1.1V

- **Eh**: emf generated between an electrode in any state & the H_2 electrode at STP, such as:

$Fe^{2+} \rightarrow Fe^{3+} + e^-$

$H^+ + e^- \rightarrow ½H_2$

$Fe^{2+} + H^+ \rightarrow Fe^{3+} + ½H_2$

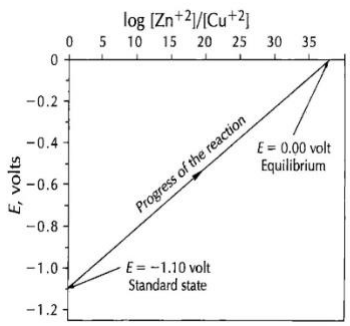
since $[H^+]=[H_2]=1.0$ in STP & $Q=K=[Fe^{3+}]/[Fe^{2+}]$

Eh =E°+(0.05916/n)log K

ΔG° = +17.75 kcal

E° = + 0.769V →

Eh=0.769+ 0.05916/log$[Fe^{3+}/Fe^{2+}]$

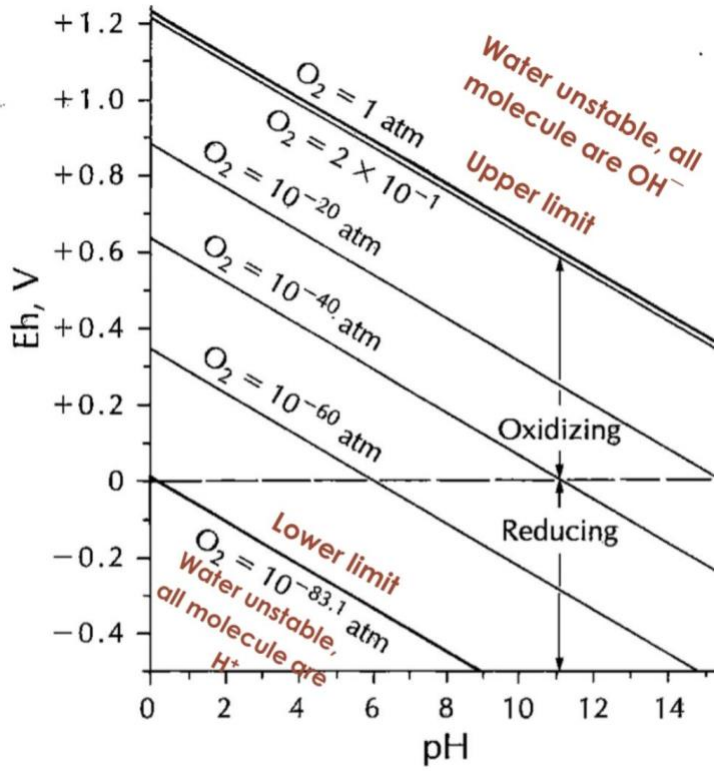


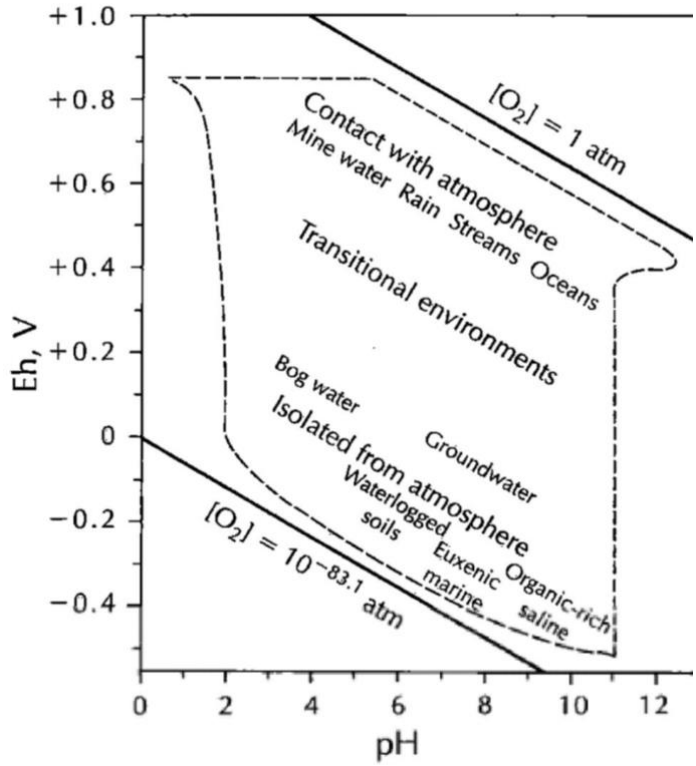
- Eh is like the pH (environmental parameter) whose values reflect the ability of the natural system to be an electron donor or acceptor
- The equation deduced above for Fe demonstrates that activity ratio $[Fe^{3+}/Fe^{2+}]$ is a function of the Eh of the environment
  - Higher Eh → oxidizing environment, high Fe^{3+}
  - Lower Eh → reducing environment

Stability field of water

At O_2 = 1atm → Eh = 1.23-0.05916 x pH

At $O_2 = 10^{-83.1}$ → Eh = -0.05916 x pH





Stability field of Fe-compounds(oxides)

Metallic iron → Magnetite Fe_3O_4

$3Fe \rightarrow Fe_3O_4 + 8e^-$ ($2Fe \rightarrow 2Fe^{3+}$, $Fe \rightarrow Fe^{2+}$)

$3Fe_{(s)} + 4H_2O_{(l)} \rightarrow Fe_3O_{4(s)} + 8H^+_{(aq)} + 8e^-$

generates emf when connected to standard H_2

$$Eh = E^\circ + \frac{0.05916}{8} log^{[H^+]^8} = E^\circ + 0.05916 log^{[H^+]}$$

ΔG° = -15.85 kcal, E° = -0.086V

Eh = -0.086 - 0.0592pH

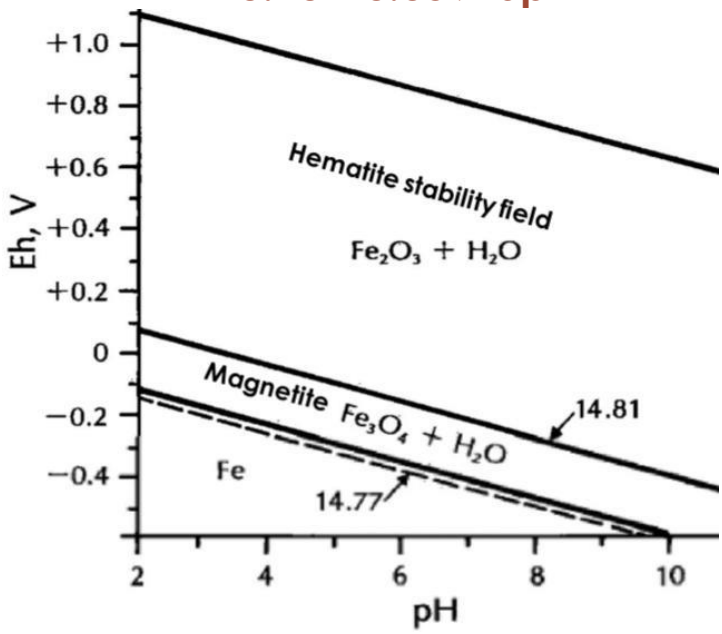
magnetite →hematite

$Fe_3O_4 \rightarrow 3Fe_2O_3 + 2e^-$

$Fe_3O_{4(s)} + H_2O_{(l)} \rightarrow 3Fe_2O_{3(s)} + H^+_{(aq)} + 2e^-$

ΔG° = +9.087 kcal, E° = +0.20V

Eh = 0.20 - 0.05916pH



- **Solubility of iron oxides :** Fe^{2+} & Fe^{3+} dominate at low pH but the solubility of iron oxides limits their stability in natural environment

Solubility of magnetite with respect to Fe^{2+}

$Fe_3O_4 + 2e^- \rightarrow 3Fe^{2+}$

$3Fe^{2+} + 4H_2O \rightarrow Fe_3O_4 + 8H^+ + 2e^-$

ΔG° = +40.698 kcal, E° = +0.88V

Eh = 0.88 + (0.05916/2) x log($[H]^8/[Fe^{2+}]^3$)

Eh = 0.88 – 0.237pH – 0.089log$[Fe^{2+}]$

$2Fe^{2+} + 3H_2O \rightarrow Fe_2O_3 + 6H^+ + 2e^-$

ΔG° = + 30.161 kcal, E° = +0.65V

Eh = 0.65 + (0.05916/2) x log($[H]^6/[Fe^{2+}]^3$)

Eh =0.65-0.177 pH – 0.0592 log$[Fe^{2+}]$

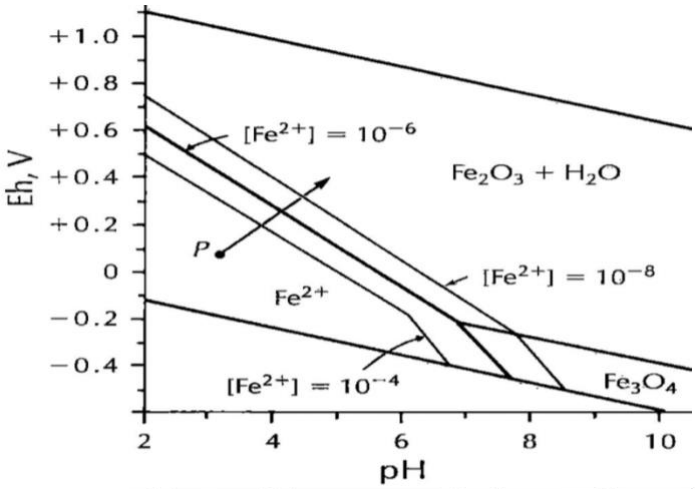
- The solubility of both oxides increases with decreasing pH & Eh, so when Hematite & magnetite are exposed to acidic environments with low Eh values (low O_2) they go into solution

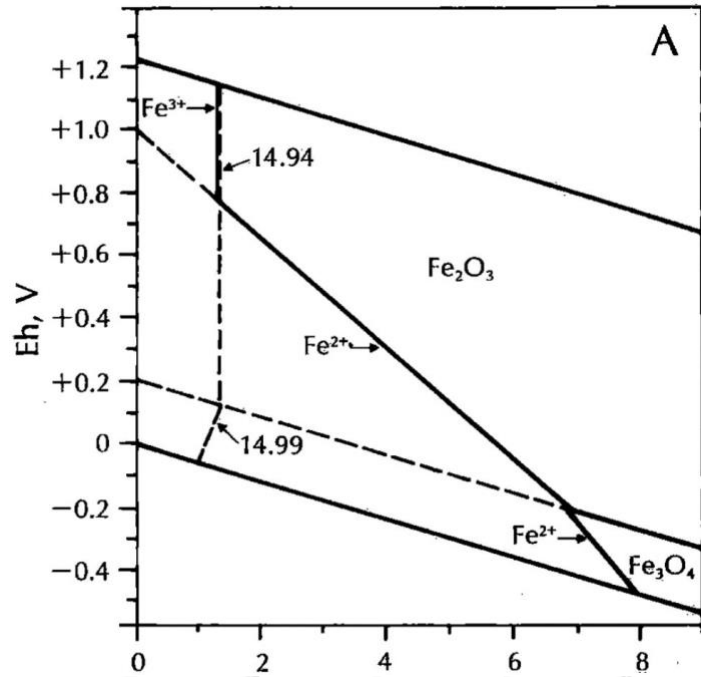
The solubility of hematite with respect to Fe^{2+} (no e^- transfer, & independent on Eh)

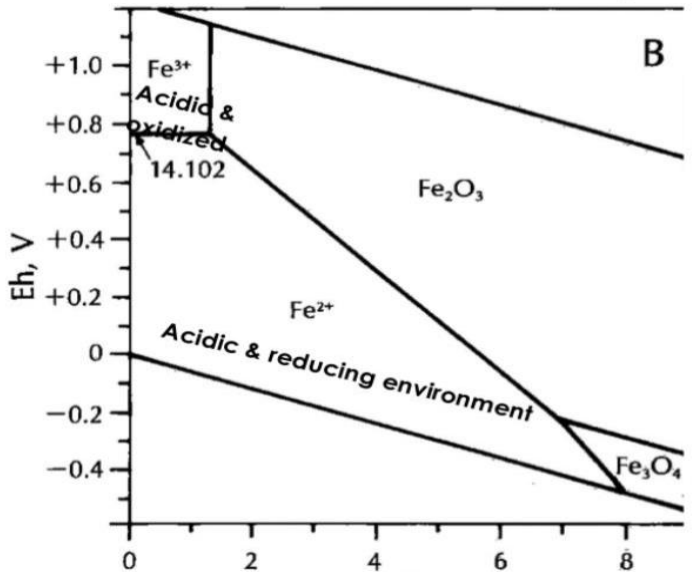
$Fe_2O_3 + 6H^+ \rightarrow 2Fe^{2+} + 3H_2O$

ΔG° = + 5.339kcal, K = $10^{-3.91}$, pH = 1.35

Eh = - 0.52 + 0.473 x pH





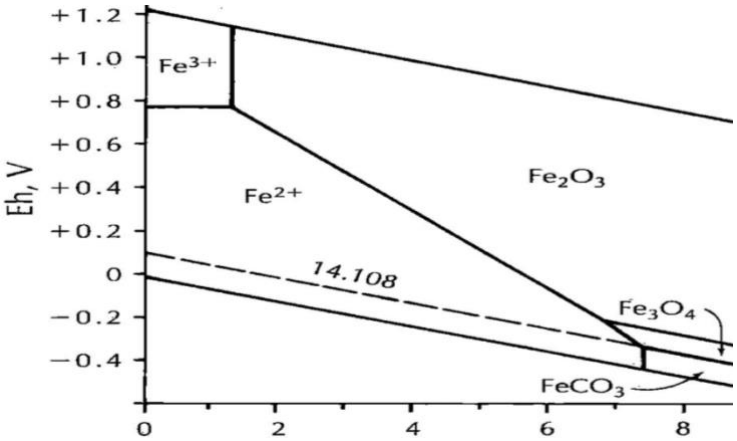


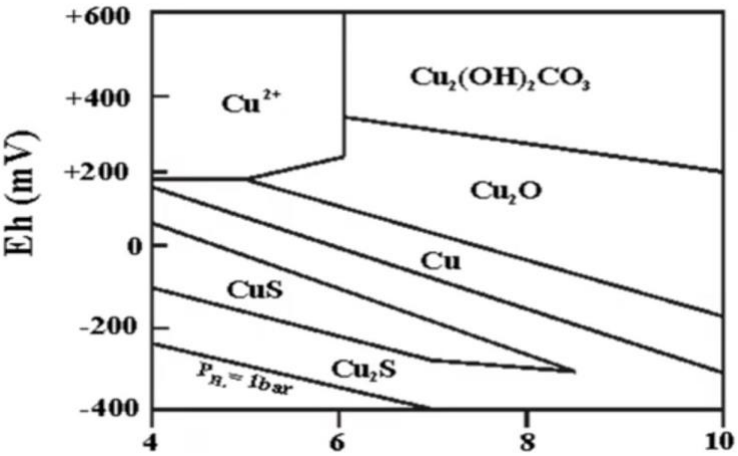
- Solution of magnetite to form Fe^{2+} involves oxidation of one divalent Fe^{2+} to Fe^{2+}

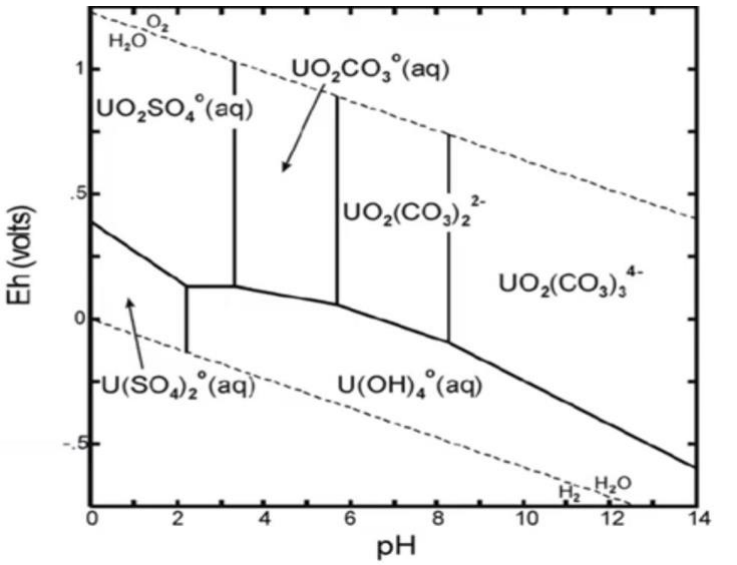
  $Fe_3O_4 + 8H^+ \rightarrow 3Fe^{3+} + 4H_2O + e-$

  ΔG° = +12.552kca, E° = +0.54V, Eh=0.77V

- Stability of siderite, magnetite, & hematite in contact with water at 25°C, $[CO_2] = 10^{-2}$ atm & activities of 10^{-6} mol/L for Fe^{2+} & Fe^{3+}







PROBLEMS

Material	ΔG°	Material	ΔG°
$H_2O_{(l)}$	-56.69	$O_{2(g)}$	0.00
$H^+_{(aq)}$	0.000	Fe^{2+}	-18.85
$PbO_{(s)}$	-45.00	$SiF_6^{2-}{}_{(aq)}$	-367.9
$PbO_{2(s)}$	-51.95	$Al_{(s)}$	0.000
$Cu_{(s)}$	+15.65	$Al^{3+}{}_{(aq)}$	-117.3
$Cu_2O_{(s)}$	-35.10	$Ag_{(s)}$	0.000
$Cu^{2+}{}_{(aq)}$	+15.65	$Ag^+{}_{(aq)}$	+18.43
$UO_2^{2+}{}_{(aq)}$	-227.9	Mn	0.000
$U^{4+}{}_{(aq)}$	-126.9	MnO(OH)	-133.2
$Cr^{3+}{}_{(aq)}$	-51.50	Mn^{2+}	-54.52
$Cr_2O_7^{2-}{}_{(aq)}$	-311.0	MnO	-86.74
$Si_{(s)}$	0.000	MnO_2	-111.2
$HF_{(l)}$	-66.64	Mn_3O_4	-306.7

Q1 Write electronic formula for S^{2-}, Ti^{4+}, P^{3-}, Zr^{4+}, Cl^{7+}

$S^{2-} \rightarrow S + 2e$ (oxidation)

$Ti^{4+} + 4e \rightarrow Ti$ (reduction)

$P^{3-} \rightarrow P + 3e$ (oxidation)

$Zr^{4+} + 4e \rightarrow Zr$ (reduction)

$Cl^{7+} + 7e \rightarrow Cl$ (reduction)

Q2 Balance the following redx reactions

a) $MnO_4^- + Cl^- \rightarrow Mn^{2+} + Cl_2$

Reaction	MnO_4^-	+	Cl^-	→	Mn^{2+}	+	Cl_2
Valance	+7,-2		-1		+2		0
Red. Half	$2Mn^{7+}$	+	10e	→	$2Mn^{2+}$		
Oxid. Half			$10Cl^-$	→	$5Cl_2$	+	10e

$2MnO_4^- + 10Cl^- + 16H^+ \rightarrow 5Cl_2 + 2Mn^{2+} + 8H_2O$

b) $As_2S_3 + NO_3^- \rightarrow HAsO_3 + S + NO$

As_2S_3	+	NO_3^-	→	$HAsO_3$	+	S	+	NO
+3,-2		+5,-2		+1,+5,-2		0		+2,-2

$2As^{3+} \rightarrow 2As^{5+} + 4e$

$3S^{2-} \rightarrow 3S + 6e$

$As_2S_3 \rightarrow 2HAsO_3 + 3S + 10e$

$N^{5+} + 3e \rightarrow N^{2+}$

$NO_3^- + 3e \rightarrow NO$

Multiply the 1st red equations in 3 & the 2nd in 10

$3As_2S_3 + 10NO_3^- \rightarrow 6HAsO_3 + 9S + 10NO$

$3As_2S_3 + 10NO_3^- + 10H^+ \rightarrow 6HAsO_3 + 9S + 10NO + 2H_2O$

c) $Cr_2O_7^{2-} + I^- \rightarrow Cr^{3+} + I_2$

$Cr_2O_7^{2-}$	+	I^-	→	Cr^{3+}	+	I_2
+6,-2		-1		+3		0

$Cr_2O_7^{2-} + 6e \rightarrow 2Cr^{3+}$

$6I^- \rightarrow 3I_2 + 6e$

$Cr_2O_7^{2-} + 6I^- \rightarrow 2Cr^{3+} + 3I_2$

$Cr_2O_7^{2-} + 6I^- + 14H^+ \rightarrow 2Cr^{3+} + 3I_2 + 7H_2O$

d) $CrO_2^- + ClO^- \rightarrow CrO_4^{2-} + Cl^-$

$2CrO_2^- + 3ClO^- + H_2O \rightarrow 2CrO_4^{2-} + 3Cl^- + 2H^+$

e) $CH_4 + SO_4^{2-} \rightarrow HCO_3^- + HS^-$

$CH_4 + SO_4^{2-} \rightarrow HCO_3^- + HS^- + H_2O$

Q4 Complete the following electrode reactions & calculate standard electrode potential

a) PbO (red) → PbO_2

$PbO_{(s)} + H_2O_{(l)} \rightarrow PbO_{2(s)} + 2H^+{}_{(aq)} + 2e^-$

$$E^\circ = \left(\frac{\Delta G^\circ}{nf}\right) = \frac{0 - 51.95 + 56.687 + 45}{2x23.06} = +1.08V$$

b) $Cu_2O \rightarrow Cu^{2+}$

$Cu_2O_{(s)} + 2H^+{}_{(aq)} \rightarrow 2Cu^{2+}{}_{(aq)} + 3e + H_2O_{(l)}$

$$E^\circ = \left(\frac{\Delta G^\circ}{nf}\right) = \frac{(2x15.65) - 56.69 + 35.10}{3x23.06} = +0.14V$$

c) $UO_2^{2+} \rightarrow U^{4+}$

$UO_2^{2+}{}_{(aq)} + 2e + 4H^+{}_{(aq)} \rightarrow U^{4+} + 2H_2O_{(l)}$

$$E^\circ = \left(\frac{\Delta G^\circ}{nf}\right) = \frac{-126.9 - 113.38 + 227.9}{2x23.06} = -0.27V$$

d) $Cr^{3+} \rightarrow Cr_2O_7^{2-}$

$Cr^{3+} + 7H_2O \rightarrow Cr_2O_7^{2-} + 3e + 14H^+$

$$E^\circ = \left(\frac{\Delta G^\circ}{nf}\right) = \frac{-311.0 + 396.83 - 15.65}{3x23.06} = +1.04$$

e) Si → SiF_6^{2-}

$Si + 6HF \rightarrow SiF_6^{2-} + 4e + 6H^+$

$E^\circ = 0.35V$

Q5 Combine the Ag & Cu electrode half-reactions & calculate the emf when $[Cu^{2+}]/[Ag^{+}]^2 = 10^{-4}$

$2Ag^{+}$ 2e → 2Ag

Cu → Cu^{2+}+ 2e

$2Ag^{+}$ + Cu → 2Ag + Cu^{2+}

ΔG° = 15.65 – 2x18.433 = - 21.22 Kcal

$$\Delta G^\circ = nfE^\circ \rightarrow E^\circ = \left(\frac{\Delta G^\circ}{nf}\right) = \frac{-21.22}{2x23.06}V = -0.46V$$

Another way: from electromotive series

$2Ag^{+}$ + 2e → 2Ag (reduction, - 0.8V)

Cu → Cu^{2+}+ 2e (oxidation, + 0.34V)

$E^\circ_{cell} = E^\circ_{oxidation} + E^\circ_{reduction}$ = 0.34 – 0.80 = - 0.46V

$$E = E + \frac{2.303RT}{nf}log^{Q} = -0.46 + \frac{0.0592log^{10^{-4}}}{2}$$

E = - 0.578V

Q6 Combine the Al & Ni electrodes & calculate the emf when $[Ni^{2+}]^3/[Al^{3+}]^2 = 10^{-2}$

$2Al^{3+}$ + 6e → 2Al (reduced, 1.70)

3Ni → $3Ni^{2+}$ + 6e (oxidation, - 0.24)

$2Al^{3+}$ + 3Ni → 2Al + $3Ni^{2+}$

$E^\circ_{cell} = E^\circ_{oxidation} + E^\circ_{reduction}$ = 1.70 – 0.24 = + 1.46V

ΔG° = (3 x – 10.9) – (2 x – 117.33) = + 202.0 Kcal

$$E^\circ = \left(\frac{\Delta G^\circ}{nf}\right) = \frac{+202.0}{6x23.06}V = +1.46V$$

$$E = 1.46 + \frac{0.0592log^{10^{-2}}}{6} = +1.44V$$

Q7 Mn forms: MnOOH, MnO, MnO_2, & Mn_3O_4

a) Determine Mn valence in each compound, & order oxides in terms of increasing valence

MnOOH	Mn	O	O	H	X = 4 – 1 = +3
	X	-2	-2	+1	
MnO	Mn	O	X = +2		
	X	-2			
MnO_2	Mn	O_2	X = +4		
	X	-4			
Mn_3O_4	MnO		Mn_2O_3	X = +3, +2	
	X	2X	-8		

$Mn^{4+}O_2$ > $Mn^{3+}O(OH)$ & $Mn^{2+}OMn^{3+}{}_2O_3$ > $Mn^{2+}O$

b) Derive Eh-pH equations based on the progressive oxidation of Mn to form oxides starting with metallic (Mn → MnO)

Mn → Mn^{2+} + 2e

$Mn_{(s)} + H_2O_{(l)} \rightarrow MnO_{(s)} + 2H^{+}_{(aq)}$ + 2e

$$E^\circ = \left(\frac{\Delta G^\circ}{nf}\right) = \frac{-86.74 + 56.69}{2x23.06}V = -0.65V$$

$$Eh = E^\circ + \frac{0.0592}{n}log^{Q} = -0.65 + \frac{0.0592}{2}log^{[H^+]^2}$$

$$Eh = -0.0592pH - 0.65 \ldots (i)$$

$3Mn^{2+}$ → Mn^{2+} + $2Mn^{3+}$ + 2e

$3MnO_{(s)} + H_2O_{(l)} \rightarrow Mn_3O_{4(s)} + 2H^{+}_{(aq)}$ + 2e

$$E^\circ = \left(\frac{\Delta G^\circ}{nf}\right) = \frac{-306.7 + 260.22 + 56.69}{2x23.06}V = +0.22V$$

$$Eh = +022 + \frac{0.0592}{2}log^{[H^+]^2}$$

$$Eh = -0.0592pH + 0.22 \ldots (ii)$$

Mn^{2+} + $2Mn^{3+}$ → $3Mn^{3+}$ + e

$Mn_3O_{4(s)} + 2H_2O_{(l)} \rightarrow 3MnO(OH)_{(s)} + H^{+}_{(aq)}$ + e

$$E^\circ = \left(\frac{\Delta G^\circ}{nf}\right) = \frac{-399.6 + 420.08}{1x23.06}V = +0.89V$$

$$Eh = +0.89 + \frac{0.0592}{1}log^{[H^+]}$$

$$Eh = -0.0592pH + 0.89 \ldots (ii)$$

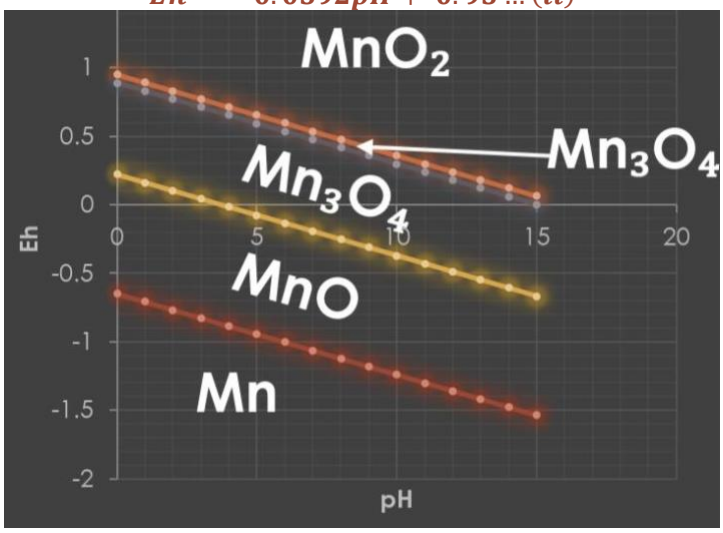
Mn^{3+} → Mn^{4+} + e

$MnO(OH)_{(s)} \rightarrow MnO_{2(s)} + H^{+}_{(aq)}$ + e

$$E^\circ = \left(\frac{\Delta G^\circ}{nf}\right) = \frac{133.2 - 111.2}{1x23.06}V = +0.95V$$

$$Eh = +0.95 + \frac{0.0592}{1}log^{[H^+]}$$

$$Eh = -0.0592pH + 0.95 \ldots (ii)$$



c) Derive equations of Eh-pH for Mn to form Mn^{2+}

MnO → Mn^{2+} + 2e, $Mn_{(s)} \rightarrow Mn^{2+}$ + 2e

$$E^\circ = \left(\frac{\Delta G^\circ}{nf}\right) = \frac{-54.52}{2x23.06}V = -1.18V$$

$$Eh = -1.18 + \frac{0.0592}{2}log^{[Mn^{2+}]} = 0.0296log^{[Mn^{2+}]} - 1.18$$

(don't controlled by pH)

ANOTHER PROBLEMS

If the measured Eh of water is 0.65, what is the dominant form of copper (Cu^{+} or Cu^{2+}) in this water (ΔG° in Kcal/mol : Cu^{+} = 11.95, Cu^{2+}= 15.65)

Cu^{+} → Cu^{2+} + e

ΔG° = 15.65 – 11.95 = +3.7Kcal

$$E^\circ = \left(\frac{\Delta G^\circ}{nf}\right) = \frac{+3.70}{1x23.06}V = +0.160V$$

$$Eh = 0.160 + \frac{0.0592}{1}log\frac{[Cu^{2+}]}{[Cu^{+}]} = 0.650$$

$$\frac{[Cu^{2+}]}{[Cu^{+}]} = 10^{\frac{(0.65-0.16)}{0.0592}} = 10^{8.3}$$ → **Cu^{+} is the dominant**

Calculate the Eh of a water with $2x10^{-3}$ Mn^{2+} & $5x10^{-10}$ Mn^{3+} activities (ΔG: Mn^{3+} = - 20.26, Mn^{2+} = - 54.52)

Mn^{2+} → Mn^{3+} + e

ΔG° = 54.52 - 20.26 = +34.26Kcal

$$E^\circ = \left(\frac{\Delta G^\circ}{nf}\right) = \frac{+34.26}{1x23.06}V = +1.49V$$

$$Eh = E^\circ + \frac{0.0592}{1}log\frac{[Mn^{+3}]}{[Mn^{+2}]} = 1.10$$

CHAPTER NINE
ISOTOPES GEOCHRONOLOGY

Types of dating in Geology	
Absolute	Actual number to describe age (date in yr)
Relative	Order of events relative to each other (older, younger, or same age)

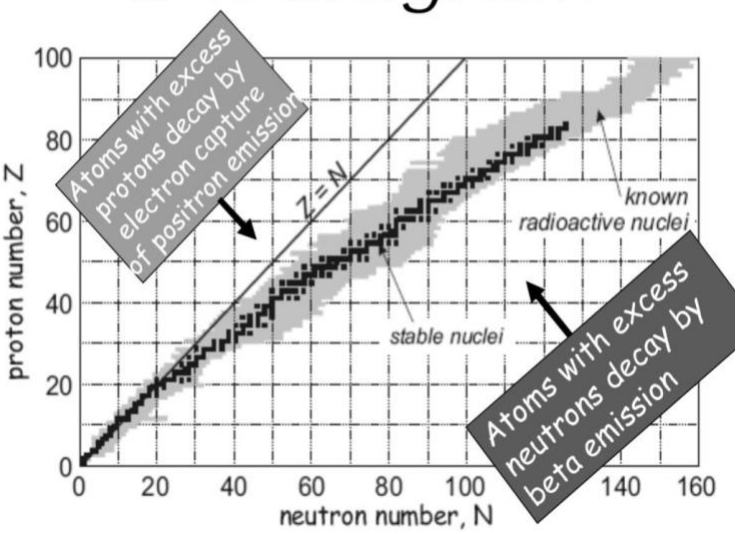
- **Radioactivity**: Spontaneous decay of element to another with concurrent release of energy
- **Atom**: The smallest possible particle that retains the properties of element (All atoms of element are essentially the same)

Particles	Mass	Charge	Positions	Controlled
Proton	✔	+ve	Nucleus	Mass of atom
Electron	✖	–ve	around nucleus	Atom volume
Neutron	✔	0	Nucleus	Mass of atom

- **Mass Number (A)**: total number of p^+ & η
- **Isotope**: atoms having different numbers of neutrons but the same number of protons

Types of isotopes	
Stable isotopes	Don't decay
Unstable isotopes	Decay into another elements, The more differences in number of p & η the more the unstable atoms

Z-N diagram



The first 20 elements (to Ca) more or less have number of η same as H^+ (related to stability)

	H^+	η	A	Z
Beta decay (β^- same as e^-)	Increase 1	Decrease 1	Constant 0	Increase 1

Formed by decay of neutron

η → H^+ + β^- + ν (antineutrino)

$$X_Z^A \rightarrow Y_{Z+1}^A + \beta^- + \nu$$

Example: $Rb_{37}^{87} \rightarrow Sr_{38}^{87} + \beta^- + \nu$

	H^+	η	A	Z
Positron (β^+, +ve e)	Decrease 1	Increase 2	Constant 0	Decrees 1

Electron capture (for atoms with a few Z)

Formed by decay of neutron

H^+ → η + β^+ + ν

$$X_Z^A \rightarrow Y_{Z-1}^A + \beta^- + \nu$$

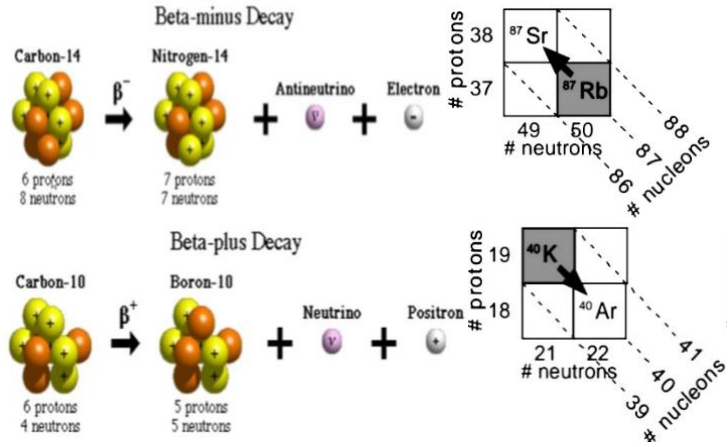
Example: $K_{19}^{40} \rightarrow Ar_{18}^{40} + \beta^+ + \nu$

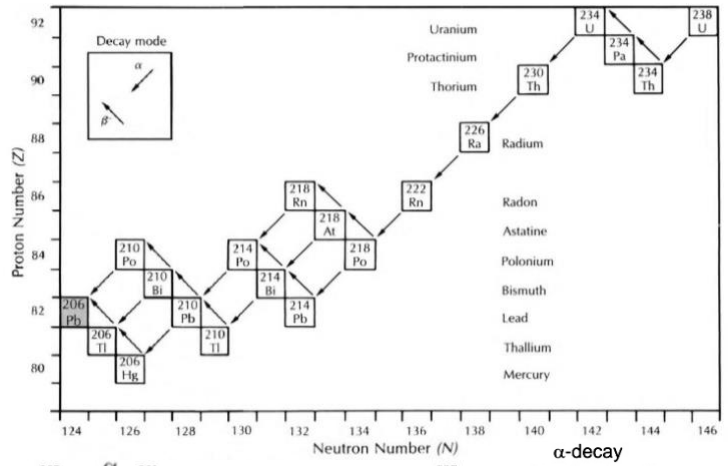
$^{50}V + e^- \rightarrow {}^{50}Ti + e^+ + \nu$

	H^+	η	A	Z
Alpha Decay (He nucleus α^{+2}, He^{+2})	Decrease 2	Decrease 2	Decrease 4	Decrease 2

For heavy atoms

$$X_Z^A \rightarrow Y_{Z-2}^{A-4} + \alpha_2^4 + E$$

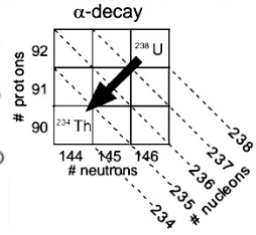




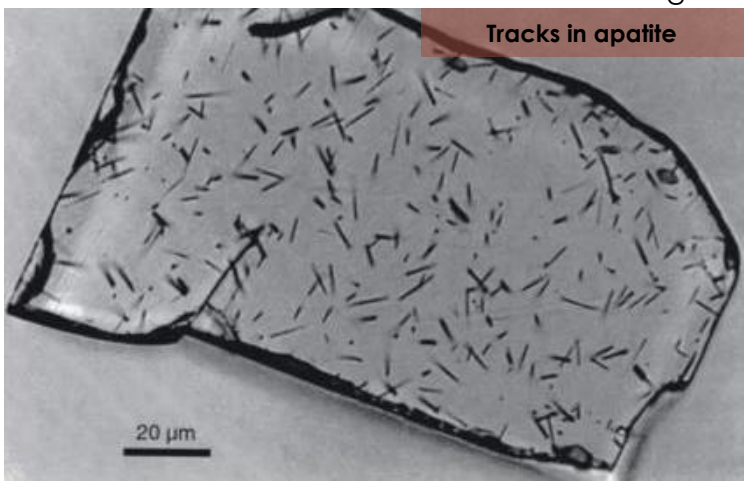
$^{235}U \xrightarrow{\alpha} {}^{231}Th$; then 7α's + 4β's later → ^{207}Pb

$^{238}U \xrightarrow{\alpha} {}^{234}Th$; then 8α's + 6β's later → ^{206}Pb

$^{232}Th \xrightarrow{\alpha} {}^{231}Ra$; then 6α's + 4β's later → ^{208}Pb



- **Absolute dating is done using** the radioactive isotopes (which decay at a constant rate)
- **Rate of decays is constant because** don't depends on any conditions (T, P, state…)
- **Nuclear Spontaneous Fission:** nucleolus breaks into 2 unequal fragments, which are unstable & decay by β-emission
  - ***heavy nuclei*** with ***even Z*** (e.g. ^{238}U, ^{244}Pu) are spontaneously fission, & with ***Odd-Z*** fission in response to η-capture
- The spontaneous fission of ^{238}U decays Energy cause damage & tracks in the crystal lattice & forms basis for ***fission-track method*** of dating



Tracks in apatite

RADIOACTIVITY EQUATIONS

- **Exponential time function**: Rate of decay is proportional to the number of atoms of that nuclide remaining at any time

$$\lambda N = -\frac{dN}{dt}$$

λ: constant, N: # of parent atoms, (-): parent atoms decreasing with t

$$by\ integration: ln^N = -\lambda t + C$$

When t=0 → $C = ln^{N_0}$

N_0 = # radioactive elements at t=0

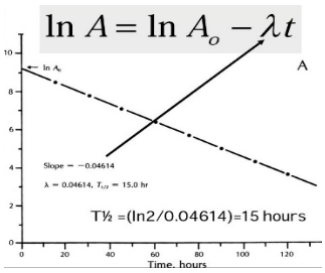
$$ln^N = -\lambda t + ln^{N_0} \rightarrow ln^{\frac{N}{N_0}} = -\lambda t \rightarrow N = N_0 e^{-\lambda t}$$

When t = half-life → $N=N_0/2$, So:

$$\frac{N_0}{2} = N_0 e^{-\lambda t_{½}} \rightarrow ½ = e^{-\lambda t_{½}} \rightarrow t_{½} = \frac{ln^2}{\lambda}$$

Example 87Rb → 87Sr with $\lambda = 1.42\times10^{-11}y^{-1}$
$t_{½} = 1n2/\ 1.42\times10^{-11}y^{-1} = 48.8Ga$

- **λ calculated experimentally:**



$$A = -\frac{dN}{dt} = \lambda N$$

$$A = A_0 e^{-\lambda t}$$

$$ln^A = ln^{A_0} - \lambda t\ (linear)$$

- we can't directly measure N_0 (inertial parent atoms) so must get expression relative to daughter atoms & remaining parent atoms

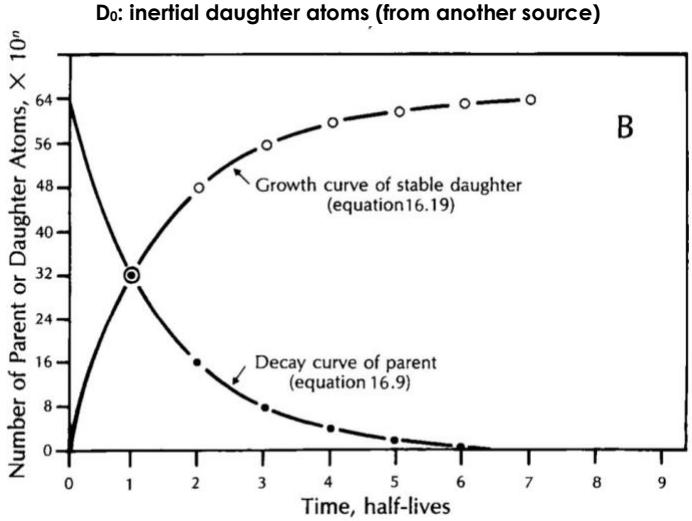
$$D^* = N_0 - N = N_0 - N_0 e^{-\lambda t} = N_0(1 - e^{-\lambda t})$$

$$D^* = N(e^{-\lambda t} - 1) \rightarrow t = \frac{1}{\lambda} ln^{\frac{D^*}{N}+1}$$

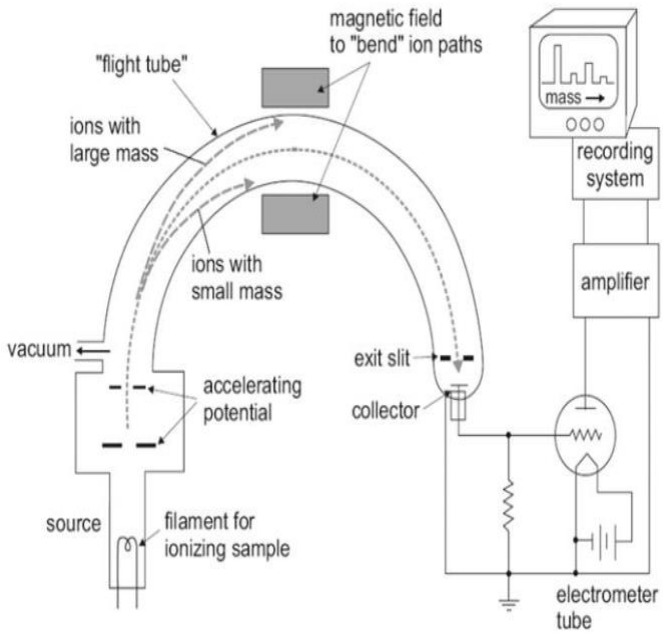
D*: radiogenic daughter atoms

$$D = D_0 + D^* = D_0 + N(e^{-\lambda t} - 1)$$

D_0: inertial daughter atoms (from another source)



- **Assumptions for age equation:**
  1. N_{parent} & $N_{daughter}$ atoms per unit weight changed by decay of parent to daughter
  2. The isotopic composition of parent element was not altered by fractionation of isotopes at time of formation of the mineral
  3. λ_{parent} is known accurately
  4. The isochron is not a mixing line
  5. The analytical data are accurate
- **Isotopes abundances measured using mass thermal ionization mass spectrometer (TIMS)**



RADIOACTIVITY METHODS

Parent N	Daughter D	t½ [yr*10¹⁰]	λ [yr⁻¹*10⁻¹⁰]	N%
K_{19}^{40}	Ar_{18}^{40}	1.19000	0.58100	0.01167
K_{19}^{40}	Ca_{20}^{40}	1.40000	4.96200	0.01167
K_{19}^{40}	$Ar_{18}^{40} + Ca_{20}^{40}$	0.12500	5.54300	0.01167
Rb_{37}^{87}	Sr_{38}^{87}	4.88000	0.14200	27.8346
Sm_{62}^{147}	Nd_{60}^{143}	10.6000	0.00654	15.0000
La_{57}^{138}	Ce_{58}^{138}	27.0000	0.02570	0.09000
La_{57}^{138}	Ba_{56}^{138}	15.1000	0.04590	0.09000
La_{57}^{138}	$Ce_{58}^{138} + Ba_{56}^{138}$	9.68000	0.07160	0.09000
Lu_{71}^{176}	Hf_{72}^{176}	3.57000	0.19400	2.60000
Re_{75}^{187}	Os_{76}^{187}	4.56000	0.15200	62.6020
U_{92}^{238}	Pb_{82}^{206}	0.44680	1.55125	99.2743
U_{92}^{235}	Pb_{82}^{207}	0.07038	9.84850	0.72000
Th_{90}^{232}	Pb_{82}^{208}	1.40100	0.49475	100.000

$Rb_{37}^{87} - Sr_{38}^{87}$ method

β-decay (Neutron capture): η → H⁺ + β⁻ + v

$$Rb_{37}^{87} \rightarrow Sr_{38}^{87} + \beta^- + \underline{\nu} + E$$

$$D = D_0 + N(e^{\lambda t} - 1)$$

$$Sr_{38}^{87} = Sr_{38\,0}^{87} + Rb_{37}^{87}(e^{\lambda t} - 1)$$

$$\left|\frac{Sr_{38}^{87}}{Sr_{38}^{86}}\right|_t = \left|\frac{Sr_{38}^{87}}{Sr_{38}^{86}}\right|_0 + \left|\frac{Rb_{37}^{87}}{Sr_{38}^{86}}\right|(e^{\lambda t} - 1)$$

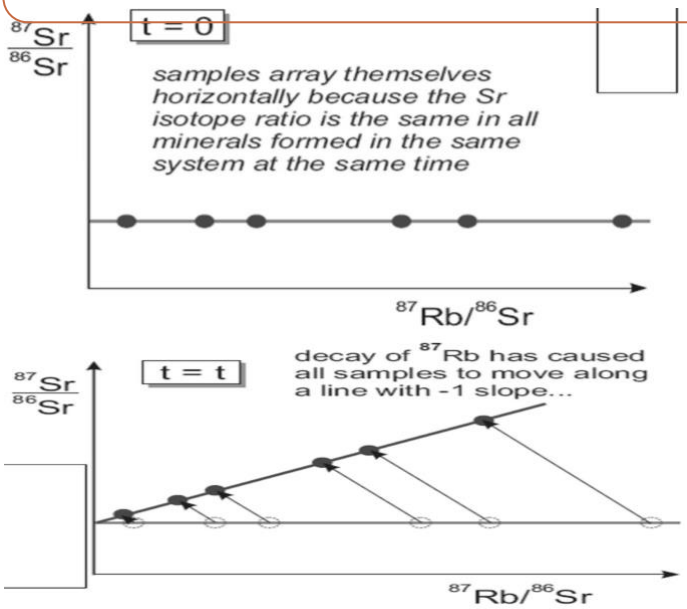
EXAMPLE calculate Rb-Sr data & half-life for biotite in gneiss if 87Rb/86Sr = 107.1, 87Sr/86Sr = 3.093, inertial 87Sr/86Sr = 0.7030, & λ = 0.142xyr⁻¹*10⁻¹⁰

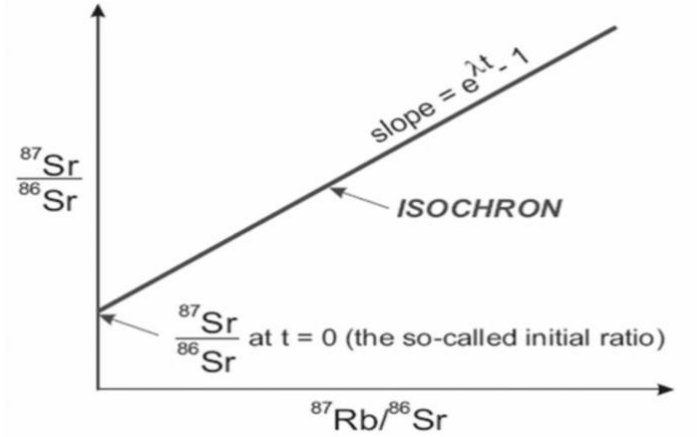
$$\left|\frac{Sr_{38}^{87}}{Sr_{38}^{86}}\right|_t = \left|\frac{Sr_{38}^{87}}{Sr_{38}^{86}}\right|_0 + \left|\frac{Rb_{37}^{87}}{Sr_{38}^{86}}\right|(e^{\lambda t} - 1)$$

$$3.093 = 0.703 + 107.1(e^{1.42x10^{-11}xt} - 1)$$

$$t = \frac{ln\left(\frac{3.093-0.703}{107.1}+1\right)}{1.42x10^{-11}} = \frac{ln^{1.02232}}{1.42}x10^{11} = 1.555Ga$$

$$t_{½} = \frac{ln^2}{\lambda} = \frac{ln^2}{1.42x10^{11}} = 48.8Ga$$



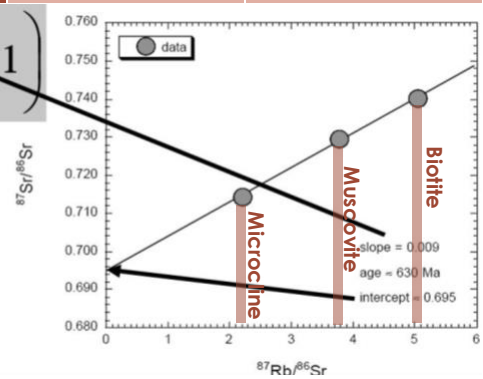


لمعرفة عدد ذرات الستريشيوم المتواجدة قبل عملية تحلل الروبيديوم نقوم باخذ عينات مختلفة من المعادن من نفس الصخر، ونقوم بتمثيلها على ال isochrone والتقاطع مع محور y هو النسبة الاولية للستريشيوم، والميل يساوي $(e^{\lambda t} - 1)$ ومنه نحسب t

EXAMPLE Minerals from igneous rocks gave the following ratios, calculate Rb-Sr data

Minerals	$Rb_{37}^{87}/Sr_{38}^{86}$	$Sr_{37}^{87}/Sr_{38}^{86}$
Biotite	5.0	0.740
Muscovite	3.8	0.729
Microcline	2.2	0.715

$$t = \frac{1}{\lambda}\ln\left(\frac{D}{N}+1\right)$$



$$slope = e^{\lambda t} - 1 = 0.009$$

$$t = \frac{ln^{slope+1}}{\lambda} = \frac{ln^{1.009}}{1.42x10^{-11}} = 6.31x10^8 yr = 631Ma$$

$Sm_{62}^{147} - Nd_{60}^{143}$ method

$$(\alpha - decay): X_Z^A \rightarrow Y_{Z-2}^{A-4} + He_2^4 + E$$

$$Sm_{62}^{147} \rightarrow Nd_{60}^{143} + \alpha + E$$

$$\left|\frac{Nd_{60}^{143}}{Nd_{60}^{144}}\right|_t = \left|\frac{Nd_{60}^{143}}{Nd_{60}^{144}}\right|_0 + \left|\frac{Sm_{62}^{147}}{Nd_{60}^{144}}\right|(e^{\lambda t} - 1)$$

- This method is useful for dating Ca-rich Precambrian igneous & metamorphic rocks

$K_{19}^{40} - Ar_{18}^{40} + Ca_{20}^{40}$ method

$$K_{19}^{40} + \beta^- \rightarrow Ar_{18}^{40}, \lambda_e = 5.81x10^{-11}a^{-1}$$

$$K_{19}^{40} \rightarrow Ca_{20}^{40} + \beta^-, \lambda_{\beta^-} = 55.43x10^{-11}a^{-1}$$

$$\left|Ar_{18}^{40}\right|_t = \left|Ar_{18}^{40}\right|_0 + \left(\frac{\lambda_e}{\lambda_e + \lambda_{\beta^-}}\right)\left|K_{19}^{40}\right|(e^{\lambda t} - 1)$$

- This method is used to date K-bearing minerals, especially the basalts of the oceanic crust

$U_{92}^{238} - Pb_{82}^{206}$ method

9σ +6β

$$\left|\frac{Pb_{82}^{206}}{Pb_{82}^{204}}\right|_t = \left|\frac{Pb_{82}^{206}}{Pb_{82}^{204}}\right|_0 + \left|\frac{U_{92}^{238}}{Pb_{82}^{204}}\right|_t (e^{\lambda_1 t} - 1)$$

$$mostly\ in\ this\ system: \left|\frac{Pb_{82}^{206}}{Pb_{82}^{204}}\right|_0 = 0, then:$$

$$t = \frac{ln\left(\frac{Pb_{82}^{206}}{U_{92}^{238}}+1\right)}{\lambda}$$

$U_{92}^{235} - Pb_{82}^{207}$ method

8σ + 4β

$$\left|\frac{Pb_{82}^{207}}{Pb_{82}^{204}}\right|_t = \left|\frac{Pb_{82}^{207}}{Pb_{82}^{204}}\right|_0 + \left|\frac{U_{92}^{235}}{Pb_{82}^{204}}\right|_t (e^{\lambda_2 t} - 1)$$

$$t = \frac{ln\left(\frac{Pb_{82}^{207}}{U_{92}^{235}}+1\right)}{\lambda}$$

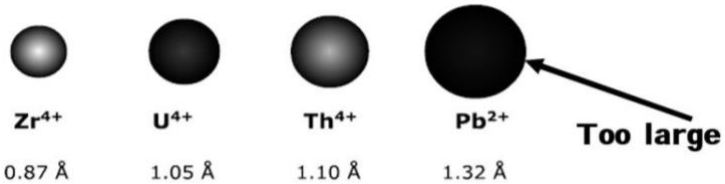
$Th_{90}^{232} - Pb_{82}^{207}$ method

7σ + 4β

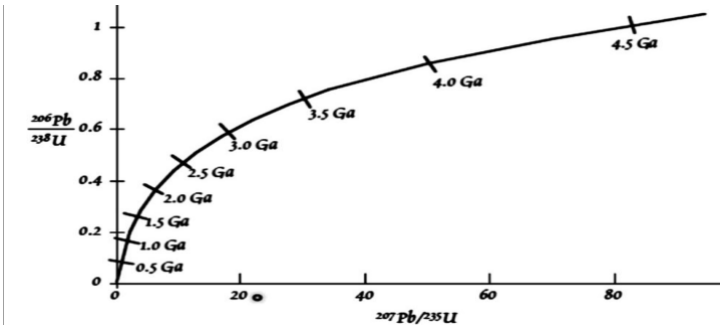
$$\left|\frac{Pb_{82}^{208}}{Pb_{82}^{204}}\right|_t = \left|\frac{Pb_{82}^{208}}{Pb_{82}^{204}}\right|_0 + \left|\frac{Th_{90}^{232}}{Pb_{82}^{204}}\right|_t (e^{\lambda_2 t} - 1)$$

$$t = \frac{ln\left(\frac{Pb_{82}^{208}}{Th_{90}^{232}}+1\right)}{\lambda}$$

- The mineral that most commonly used in U-Pb & Th-Pb methods is zircon ($ZrSiO_4$) because U^{4+} & Th^{4+} rabidly substitute for Zr^{4+} because have same radius & charge but led are too large

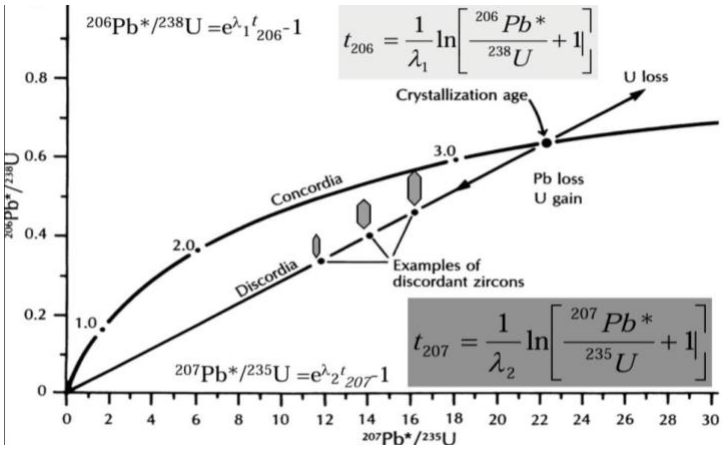


بتعويض ال t في المعادلتين Pb-207Pb206 نحصل على Concordia diagram (يستخدم بتحديد اعمار الزيركون بناء على Pb/U ratios)



ولكن عند اخذ عينات متعددة من المعادن من نفس الصخر واسقاطها على ال diagram وجد انها تقع على خط مستقيم بعيد عن ال Concordia line ويسمى discordia وتم تفسير ذلك بانه خلال حدوث geological events مثل metamorphism, change in T, & during uplift يحدث diffusion للرصاص (اي يقل العمر المفترض وهو ما يسمى lead loss of time) والعينات الاصغر تفقد رصاص اكثر لذا كلما قل حجم العينة تبتعد اكثر عن ال Concordia ويوجد نقطتي تقاطع بين ال concordia & discordia وهما:

1. التقاطع من الاعلى: وهو العمر الاصلي للعينات (الصخر)
2. التقاطع من الاسفل: وهو عمر ال events



PROBLEMS

Calculate Rb-Sr date for the sample of biotite if 87Rb/86Sr = 107.1, 87Sr/86Sr = 3.093, (87Sr/86Sr)0 = 0.7030, & Decay constant λ = 1.42x10^{-11}a^{-1}

$$\left|\frac{Sr_{38}^{87}}{Sr_{38}^{86}}\right|_t = \left|\frac{Sr_{38}^{87}}{Sr_{38}^{86}}\right|_0 + \left|\frac{Rb_{37}^{87}}{Sr_{38}^{86}}\right| (e^{\lambda t} - 1)$$

$$3.093 = 0.7030 + 107.1(e^{1.42x10^{-10}xt} - 1)$$

$$t = \frac{ln\frac{3.093-0.703}{107.1}+1}{1.42x10^{-11}} = 1.55x10^9 yr = 1.55Ga$$

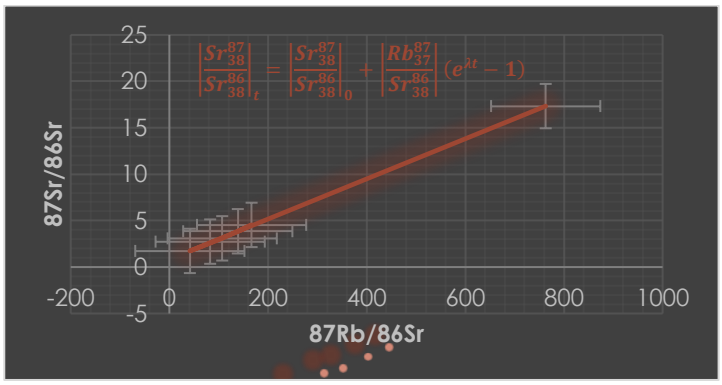
Calculate the slope & intercept of Rb-Sr isochron by least squares method using the following data

Samples	87Rb/86Sr	87Sr/86Sr
1	763.00	17.337
2	41.520	1.7390
3	107.12	3.0930
4	166.70	4.5430
5	138.70	3.8580
6	330.70	3.0570
7	82.700	2.7410

Use the slope to calculate a date for these samples (λ = 1.42x10^{-11})

Note that, we use this method when we don't know $(87Sr)_0$

Note that, least squares method is a statistical method used to draw the best fit line (excel sheet basically use this method)



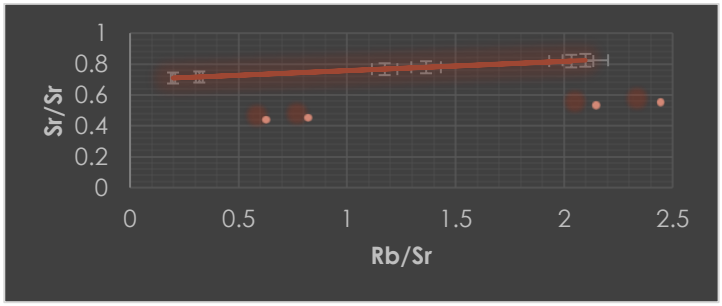
Intercept = 0.8806 = $(87Sr/86Sr)_0$

slope = 0.0216 = $(e^{\lambda t} - 1)$

$$t = \frac{ln^{1.0216}}{1.42x10^{-11}} = 1.5Ga$$

Calculate the Rb-Sr age & initial 87Sr/86Sr of a sample based on the following data (λ =1.42x10^{-11})

Samples	87Rb/86Sr	87Sr/86Sr
1	2.098	0.8245
2	0.198	0.7096
3	1.173	0.7668
4	2.033	0.8191
5	1.364	0.7791
6	0.319	0.7163



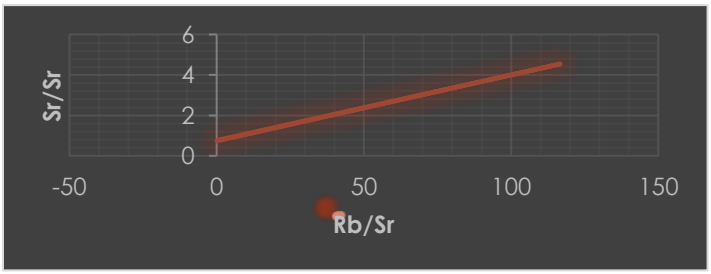
Intercept = $(87Sr/86Sr)_0$ = 0.6971

$$(e^{\lambda t} - 1) = slope = \frac{0.8245 - 0.7096}{2.098 - 0.198} = 0.0605$$

$$t = \frac{ln^{1.0605}}{1.42x10^{-11}} = 4.14Ga$$

Calculate a Rb-Sr date from the following analyses (λ =1.42x10^{-11})

Samples	87Rb/86Sr	87Sr/86Sr
Whole rock	1.1730	0.7668
Biotite	116.74	4.5430
K-feldspar	0.6437	0.7822
Plagioclase	0.0633	0.7344



$(87Sr/86Sr)_0$ = 0.7468

$$(e^{\lambda t} - 1) = 0.02277 \rightarrow t = 1.59Ga$$

Calculate U-Pb & Th-Pb dates if: $^{206}Pb/^{204}Pb$ = 53.90, $^{207}Pb/^{204}Pb$ = 20.76, $^{208}Pb/^{204}Pb$ = 36.94, $^{238}U/^{204}Pb$ = 88.746, $^{238}U/^{235}U$ = 137.88, $^{232}Th/^{204}Pb$ = 55.38, $(^{206}Pb/^{204}Pb)i$ = 12.97, $(^{207}pb/^{204}pb)i$ = 14.17, $(^{208}pb/^{204}pb)i$ = 33.90, $\lambda 1$ =1.55125x10^{-10}, $\lambda 2$ = 9.8485x10^{-10}, & $\lambda 3$ = 4.9475x x10^{-11}

$$\left|\frac{Pb_{82}^{206}}{Pb_{82}^{204}}\right|_t = \left|\frac{Pb_{82}^{206}}{Pb_{82}^{204}}\right|_0 + \left|\frac{U_{92}^{238}}{Pb_{82}^{204}}\right|_t (e^{\lambda_1 t} - 1)$$

$$t_{206} = \frac{ln^{\frac{53.90-12.97}{88.746}+1}}{1.55125x10^{-10}} = 2.44Ga$$

$$\frac{\frac{U^{238}}{Pb^{204}}}{\frac{U^{238}}{U^{235}}} = \frac{U^{235}}{Pb^{204}} = \frac{88.746}{137.88} = 0.643$$

$$\left|\frac{Pb_{82}^{207}}{Pb_{82}^{204}}\right|_t = \left|\frac{Pb_{82}^{207}}{Pb_{82}^{204}}\right|_0 + \left|\frac{U_{92}^{235}}{Pb_{82}^{204}}\right|_t (e^{\lambda_2 t} - 1)$$

$$t_{207} = \frac{ln^{\frac{20.76-14.17}{0.643}+1}}{9.8485x10^{-10}} = 2.458Ga$$

$$\left|\frac{Pb_{82}^{208}}{Pb_{82}^{204}}\right|_t = \left|\frac{Pb_{82}^{208}}{Pb_{82}^{204}}\right|_0 + \left|\frac{Th_{90}^{232}}{Pb_{82}^{204}}\right|_t (e^{\lambda_2 t} - 1)$$

$$t_{208} = \frac{ln^{\frac{36.94-33.90}{55.38}+1}}{4.9475x10^{-11}} = 1.08Ga$$

Calculate 3 dates for a zircon by the following data: $^{238}U/^{204}Pb$ = 6807.4, $^{235}U/^{204}Pb$ = 49.372, $^{232}Th/^{204}Pb$ = 2829.4, $^{206}Pb/^{204}Pb$ = 1657.29, $^{207}Pb/^{204}Pb$ = 171.99, $^{208}Pb/^{204}Pb$ =185.72, λ_{206} =1.55125x10^{-10}, λ_{207} = 9.8485x10^{-10}, λ_{208} = 4.9475x x10^{-11}

$$t = \frac{ln^{\left(\frac{Pb_{82}^{206}}{U_{92}^{238}}+1\right)}}{\lambda} = \frac{1}{\lambda} x ln^{\frac{\left(\frac{Pb^{206}}{Pb^{204}}\right)}{\left(\frac{U^{235}}{Pb^{204}}\right)}+1}$$

$$t = \frac{10^{10}}{1.55125} x ln^{\left(\frac{1657.29}{6807.4}+1\right)} = 1.4Ga$$

$$t = \frac{ln^{\left(\frac{Pb_{82}^{207}}{U_{92}^{235}}+1\right)}}{\lambda} = \frac{ln^{\left(\frac{\left(\frac{Pb^{207}}{Pb^{204}}\right)}{\left(\frac{U^{235}}{Pb^{204}}\right)}+1\right)}}{\lambda}$$

$$t_{207} = \frac{10^{10}}{9.8485} ln^{\frac{171.99}{49.372}+1} = 1.5Ga$$

$$t = \frac{ln^{\left(\frac{Pb_{82}^{208}}{Th_{90}^{232}}+1\right)}}{\lambda} = \frac{1}{\lambda} ln^{\left(\frac{\left(\frac{Pb^{208}}{Pb^{204}}\right)}{\left(\frac{Th^{232}}{Pb^{204}}\right)}+1\right)}$$

$$t_{208} = \frac{10^{11}}{4.9475} ln^{\left(\frac{185.72}{2829.4}+1\right)} = 1.3Ga$$

CHAPTER TEN
STABLE ISOTOPES

- The Earth has a unique position in the solar system because H_2O exists in the liquid form
  - This existence is a pre-requisite for the development & preservation of life
  - The medium, where chemical reactions take place; & from which a series of solids form, like carbonates, silicates, phosphates
- Oxygen is the most abundant element in the Earth's crust & H in the solar system
- H, O, C, N, & S share in all geochemical & biochemical reactions on the Earth's surface
  - The masses of these elements in addition to Li, B, Si, Cl, & Se are subject to mass-dependent fractionation

Fractionation due to mass differences							
Isotope	H D	^{12}C ^{13}C	^{14}N ^{15}N	^{16}O ^{18}O	^{32}S ^{34}S	^{235}U ^{238}U	^{206}Pb ^{207}Pb
D%	99.8	8.36	7.12	12.5	6.24	1.30	0.49

Abundances of stable H, & O isotopes					
Elements	Hydrogen		Oxygen		
Isotopes	H_1^1	H_1^2	O_8^{16}	O_8^{17}	O_8^{18}
Abundance	99.985%	0.015	99.762	0.038%	0.2%
Mw [amu]	1.0078	2.014	15.995	16.999	17.999

- The energy of a diatomic molecule is a function of its vibrational frequency (v):

  $E = ½hv$, h (Plank's constant) = 5.626176×10^{-34} J/Hz
- When a light isotope is replaced by a heavier one in a diatomic molecule, the vibrational frequency decreases; which results in the energy of the molecule
  - This decrease in the energy results in strengthening the covalent bond
  - A consequence of molecule containing the heavy isotope are more stable & less reactive than those with the light ones
- The masses of isotopes determine the velocities of molecules of a particular gas at a given T
  - all molecules of an ideal gas have the same kinetic energy at specified T: $E_K = ½mv^2$

So 2 isotopic varieties of a molecule having different masses have the same kinetic energy, then:

$$½m_H v_H^2 = ½m_L v_L^2 \ \& \ \frac{v_L}{v_H} = \left(\frac{m_h}{m_L}\right)^{½}$$

$m_h/m_L > 1$ (i.e. $v_L/v_H > 1$)

For 12C 16O & 13C 16O

$$\frac{v_L}{v_H} = \left(\frac{m_h}{m_L}\right)^{½} = \left(\frac{28.998}{27.995}\right)^{½} = 1.0178$$

- The existence of 2H stable isotopes & 3O stable isotopes makes 9 different combinations of water molecule (The masses range from 18.010565 to 22.02716amu):

  $H_2{}^{16}O$, $H_2{}^{17}O$, $H_2{}^{18}O$
  $HD^{16}O$, $HD^{17}O$, $HD^{18}O$
  $D_2{}^{16}O$, $D_2{}^{17}O$, $D_2{}^{18}O$

  The difference between $D_2{}^{18}O$ & $H_2{}^{16}O$ = 22.3%

MATHEMATICAL RELATIONS

- The isotopic composition of all isotopes that are affected by fractionation is expressed by the parameter R $\boldsymbol{R} = \frac{Heavy(H)}{Light\ (l)}$

EXAMPLE for 18O & 16O (A%: 18O: 0.2, 16O: 99.762)

$$R = \frac{Heavy(H)}{Light\ (l)} = \frac{O^{18}}{O^{16}} = \frac{0.2}{99.762} = 2.005x10^{-3}$$

- The isotopic composition of oxygen & hydrogen are measured by mass spectrometry & expressed relative to ***SMOW*** {Standard Mean Oceanic Water}
- **Delta Notation (δ):** The differences in isotopic ratios (are relatively small & expressed as parts per thousand, deviations from a standard)

$$\delta_x = \frac{R_x - R_{standard}}{R_{standard}} x1000‰$$

Relative to a standard (oceanic water)	
+ve	The sample is enriched in the heavy isotopes
-ve	The sample is depleted in the heavy isotopes

- When water evaporates at equilibrium under constant P, isotopic composition of the vapor differs from that of the remaining water due to isotope fractionation during the evaporation
- **Fractionation factor**: The extent of fractionation

$$\alpha_b^a = \frac{R_a}{R_b} \rightarrow for\ H_2O_{(g)}: \alpha_{vapor}^{liquid} = \frac{R_l}{R_v}$$

$$\alpha_v^l(O) = \frac{R_l}{R_v} = \frac{(O^{18}/O^{16})_l}{(O^{18}/O^{16})_v} = 1.0098$$

$$\alpha_v^l(H) = \frac{R_l}{R_v} = \frac{(D/H)_l}{(D/H)_v} = 1.84$$

- fractionation factors decrease with increasing temperatures & approach a value of 1
- In case of isotope fractionation between 2 phases a & b in isotopic equilibrium, the isotope composition of element in phase a & b are:

$$\delta_a = \frac{R_a - R_{standard}}{R_{standard}} x1000‰ \ \& \ \delta_b = \frac{R_b - R_{standard}}{R_{standard}} x1000‰$$

$$R_a = R_s(\delta_a + 10^3)x10^{-3} \& \ R_b = R_s(\delta_b + 10^3)x10^{-3}$$

Then:

$$\alpha_b^a = \frac{R_a}{R_b} = \frac{R_s(\delta_a + 10^3)x10^{-3}}{R_s(\delta_b + 10^3)x10^{-3}} = \frac{\delta_a + 1000}{\delta_b + 1000}$$

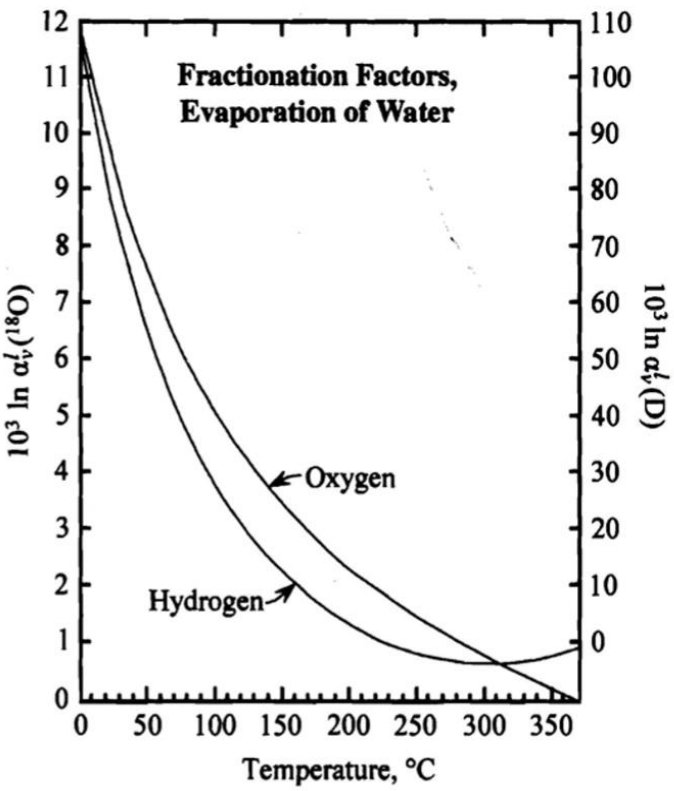
$$ln\,[\alpha_b^a] \approx \frac{1}{T\,[°C]}$$

$$10^3 ln^{\alpha_b^a} \approx 10^3(\alpha_b^a - 1) \approx \Delta_{a-b}$$

$$\Delta_{a-b} \approx \delta_b - \delta_a = \frac{A}{T^2} x10^6 + B$$

METEORIC PRECIPITATION

- lightest water (**$H_2{}^{16}O$**) evaporates preferentially relative to the heaviest molecule (**$D_2{}^{18}O$**)
- heaviest molecule in water vapor condenses preferentially relative to lightest molecule, so:
  - depleted in D & ^{18}O relative to sea water
  - Condensate enriched in D & ^{18}O relative to the vapor



EXAMPLE If you've got a sample of water vapor from an ocean, the water T is 20°C, calculate the delta Notation (δ) for 18O & D in this sample using the previous diagram

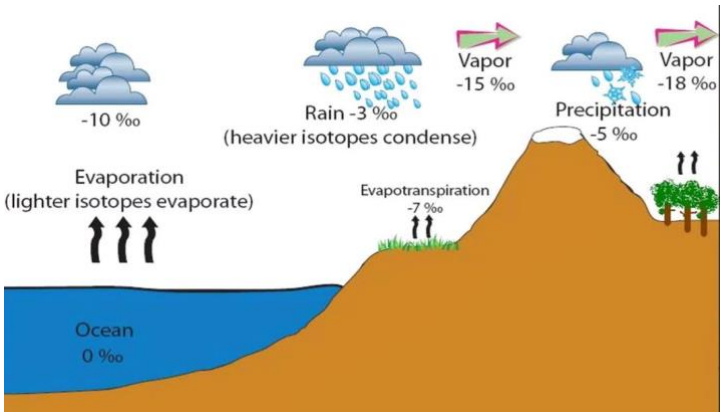
$$at 20°C: 10^3 ln^{\alpha_v^l(O)} = 9.7702 \rightarrow \alpha_v^l(O) = 1.00982$$

$$at 20°C: 10^3 ln^{\alpha_v^l(D)} = 80.9855 \rightarrow \alpha_v^l(D) = 1.08436$$

$$\alpha_v^l(O^{18}) = \frac{\delta_l + 1000}{\delta_v + 1000} = \frac{1000}{\delta_v + 1000} (because\ L = St)$$

$$\delta_v(O) = \frac{1000}{1.0098} - 1000 = -9.70‰$$

$$\delta(D) = \frac{1000}{1.084} - 1000 = -77.49‰$$



مع الوقت يقل ال O18 (يسقط على هيئة امطار) لان النظائر الاثقل حركتها اقل من النظائر الاخف وروابطها اقوى

نستفيد من هذه الدراسات في تاريخ الارض من خلال دراسة الجليد القديم حيث نقوم باستنتاج درجات الحرارة عبر العصور (التغير المناخي والمناخ القديم)

PROBLEMS

- Calculate $\delta^{18}O$ of water vapor in equilibrium with liquid water at 10°C assuming $\delta^{18}O_l$ = -10.0% (SMOW) & α^v_l = 1.0105

$$\alpha_v^l = \frac{R_l}{R_v} = \frac{\delta_l + 1000}{\delta_v + 1000} = 1.0105$$

$$\frac{-10 + 1000}{\delta_v + 1000} = 1.0105$$

$$\delta_v = -20.3‰$$

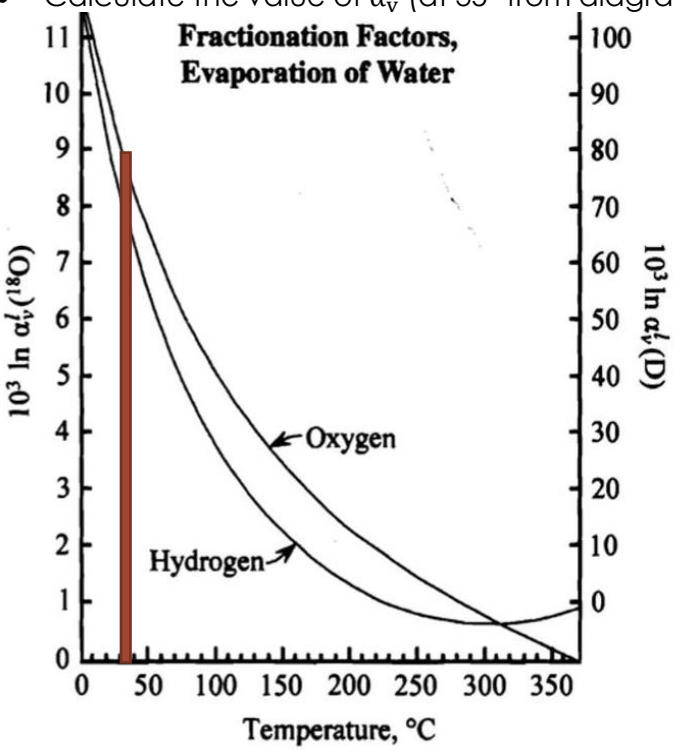
- Calculate $\delta^{18}O$ of liquid water vapor in equilibrium with vapor water at 10°C assuming $\delta^{18}O_g$ = -25.0% (SMOW) & α^v_l = 1.0105 (—14.8‰)

$$\alpha_v^l = \frac{R_l}{R_v} = \frac{\delta_l + 1000}{\delta_v + 1000}$$

$$\alpha_v^l = \frac{\delta_l + 1000}{-25 + 1000} = 1.0105$$

$$\delta_l = -14.8‰$$

- Calculate the value of α_v^l (at 35° from diagram)



$$at\ 35°\ 10^3 ln\alpha_v^l(^{18}O) \approx 8.0 \rightarrow \alpha_v^l = 1.00803$$