Inorganic Chemistry

Second year
1st semester

Lecture 1

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To build up an atomic structure we should follow the rules:

1- Pauli principal : No two electrons in the same orbital can have the same four quantum no.s only electrons with opposite spin can occupy the same orbital.

2- Hund's rule : Electrons fill degenerate orbitals one at a time before doubling up in the same orbital"

The p,d,f,g orbitals sets are equivalent in energy but differ in orientation in space **ml=(2*l*+1)**

p(3) , d(5) ,f(7), g(9) . So they should be half filled before any are filled to avoid electron-electron repulsion as repulsion means high energy

3- <u>Aufbau Principle</u> states that:

> ***“The orbitals of lower energy are filled first with the electrons then the orbitals of high energy are filled.”***

The orbital energy does not depend on value of n only but also on l , using (n + l) rule , the lower energy orbital is that of lower value of (n + l) . If (n + l) values of different orbitals are equal the one with the lowest value of n fill first

S- block elements
IA and IIA

Group 1 - elements with only one valence electron: These are called the Alkali-Metal Group

Electronic configuration

^{3}Lithium	Li	{He}2s^{1}
^{11}Sodium	Na	{Ne}3s^{1}
^{19}Potassium	K	{Ar}4s^{1}
^{37}Rubidium	Rb	{Kr}5s^{1}
^{55}Cesium	Cs	{Xe}6s^{1}
^{87}Francium	Fr	{Rn}7s^{1}

Physical Properties

metals i.e good conductors, soft, low melting point and boiling point

S- block elements
IA and IIA

Group 2 - *The Alkaline Earth Metals(IIA)*

			electron configuration
beryllium	Be	Z= 4	[He] $2s^2$
magnesium	Mg	12	[Ne] $3s^2$
calcium	Ca	20	[Ar] $4s^2$
strontium	Sr	38	[Kr] $5s^2$
barium	Ba	56	[Xe] $6s^2$
radium	Ra	88	[Rn] $7s^2$

The last element, radium, is radioactive and will not be considered here.

Deviation from (n+ ℓ) rule

In some main transition elements and inner transition elements some deviation from (n + l) rule is observed

The interaction between the two Cr and Cu in 1st tr. Series electrons in 4S orbital is of high energy (paring energy) this effect places an extra electron to 3d level and remove from 4s causing

$_{24}$Cr [Ar] $3d^5$ $4s^1$(half-filled orbitals)
$_{29}$Cu [Ar] $3d^{10}$ $4s^1$(half-filled s-orbitals and full d-orbitals)

The difference in energy between an orbital of 2e and 1e can be explained as the pairing energy is higher than energy gap between ns & (n-1)d as the value of Z* increase the energy of shells decreases

Main transition elements (d-block)

- Main transition elements (d-block) take their collective name from their role as a bridge between the chemically active metals of gr. IA & IIA and much less active metals of gr. 12(Zn family) , 13(Boron family) , 14(Carbon family) .

- As s-block elements are metallic in nature and p-block elements are non-metallic, hence d-block elements show a transition from metallic to non-metallic nature. In other words, they show a transition from most electropositive s-block elements to least electropositive or most electronegative p-block elements.

- The elements $_{30}Zn$, $_{48}Cd$, $_{80}Hg$ (gr. 12) have unique properties , while they resemble the alkaline earth metals IIA in giving oxidation state of (+2) , they differ from IIA of having higher Z* and more polarizing effect

1st transition element series : A part of (Period 4)
[Ar] $3d^{1-10}$ $4s^{1-2}$ This is also called as 3d series

Sc	(Z = 21)	[Ar] $3d^1 4s^2$
Ti	(Z = 22)	[Ar] $3d^2 4s^2$
V	(Z = 23)	[Ar] $3d^3 4s^2$
Cr	(Z = 24	* [Ar] $3d^5 4s^1$
Mn	(Z = 25)	[Ar] $3d^5 4s^2$
Fe	(Z = 26)	[Ar] $3d^6 4s^2$
Co	(Z = 27)	[Ar] $3d^7 4s^2$
Ni	(Z = 28	[Ar] $3d^8 4s^2$
Cu	(Z = 29)	*[Ar] $3d^{10} 4s^1$
Zn	(Z = 30)	[Ar] $3d^{10} 4s^2$ (non Tr.)

* Deviate from($n+l$)

Second transition series: A part of (period 5) : [Kr] $4d^{1-10}$ $5s^{1-2}$

This is also called as 4d series

Element	Atomic Number	Symbol	Electronic configuration
Yttrium	39	Y	[Kr] $4d^1$ $5s^2$
Zirconium	40	Zr	[Kr] $4d^2$ $5s^2$
Niobium	41	Nb	*[Kr] $4d^4$ $5s^1$
Molybdenum	42	Mo	*[Kr] $4d^5$ $5s^1$
Technetium	43	Tc	?[Kr] $4d^5$ $5s^2$
Ruthenium	44	Ru	*[Kr] $4d^7$ $5s^1$
Rhodium	45	Rh	*[Kr] $4d^8$ $5s^1$
Palladium	46	Pd	*[Kr] $4d^{10}$ $5s^0$
Silver	47	Ag	*[Kr] $4d^{10}$ $5s^1$
Cadmium(non Tr.)	48	Cd	[Kr]$4d^{10}$ $5s^2$

* Deviate from($n+\ell$) ; ? May have [Kr] $4d^6$ $5s^1$

Third Transition Series

It is a part of period 6 : [Xe] $4f^{14}$ $5d^{1-10}$ $6s^{1-2}$ except La [Xe] $4f^0$ $5d^1$ $6s^2$? Lanthanum and Hafnium to Mercury This is also called as 5d series

Element	Atomic number	Symbol	Electronic configuration
Lanthanum	57	La	*[Xe] $4f^0$ $5d^1$ $6s^2$?
Hafnium	72	Hf	[Xe] $4f^{14}$ $5d^2$ $6s^2$
Tantalum	73	Ta	[Xe] $4f^{14}$ $5d^3$ $6s^2$
Tungsten	74	W	[Xe] $4f^{14}$ $5d^4$ $6s^2$
Rhenium	75	Re	[Xe] $4f^{14}$ $5d^5$ $6s^2$
Osmium	76	Os	[Xe] $4f^{14}$ $5d^6$ $6s^2$
Iridium	77	Ir	[Xe] $4f^{14}$ $5d^7$ $6s^2$
Platinum	78	Pt	*[Xe] $4f^{14}$ $5d^9$ $6s^1$?
Gold	79	Au	*[Xe] $4f^{14}$ $5d^{10}$ $6s^1$?
Mercury(non Tr.)	80	Hg	[Xe] $4f^{14}$ $5d^{10}$ $6s^2$

* Deviate from(n+*l*

Inner transition elements

The elements in which the additional electrons enters (n-2)f orbitals are called **inner transition elements**. The valence shell electronic configuration of these elements can be represented as **$\underline{(n-2)f}^{0-14}\ \underline{(n-1)d}^{0-1}\ \underline{ns}^{2}$.**

4f inner transition metals are known as lanthanides because they come immediately after lanthanum and 5f inner transition metals are known as actinoids because they come immediately after actinium.

Electronic Configuration of Lanthanoids (part of period period 6)

Element name	Symbol	Z	M	Ln $^{3+}$	r (Ln $^{3+}$ / pm)
Lanthanum	La	57	*$[Xe]\ 5d^1\ 6s^2$	$[Xe]4f^0$	116
Cerium	Ce	58	*$[Xe]4f^1 5d^1\ 6s^2$	$[Xe]4f^1$	114
Praesodymium	Pr	59	$[Xe]4f^3 6s^2$	$[Xe]4f^2$	113
Neodymium	Nd	60	$[Xe]4f^4 6s^2$	$[Xe]4f^3$	111
Promethium	Pm	61	$[Xe]4f^5 6s^2$	$[Xe]4f^4$	109
Samarium	Sm	62	$[Xe]4f^6 6s^2$	$[Xe]4f^5$	108
Europium	Eu	63	$[Xe]4f^7 6s^2$	$[Xe]4f^6$	107
Gadolinium	Gd	64	*$[Xe]4f^7\ 5d^1 6s^2$	$[Xe]4f^7$	105
Terbium	Tb	65	$[Xe]\ 4f^9 6s^2$	$[Xe]4f^8$	104
Dysprosium	Dy	66	$[Xe]\ 4f^{10} 6s^2$	$[Xe]4f^9$	103
Holmium	Ho	67	$[Xe]\ 4f^{11} 6s^2$	$[Xe]4f^{10}$	102
Erbium	Er	68	$[Xe]\ 4f^{12} 6s^2$	$[Xe]4f^{11}$	100
Thulium	Tm	69	$[Xe]\ 4f^{13} 6s^2$	$[Xe]4f^{12}$	99
Ytterbium	Yb	70	$[Xe]\ 4f^{14} 6s^2$	$[Xe]4f^{13}$	99
Lutetium	Lu	71	$[Xe]\ 4f^{14}\ 5d^1\ 6s^2$	$[Xe]4f^{14}$	98

- Or $[Xe]4f^2\ 6s^2$ *deviates from ($n+\ell$)

Electronic configuration of Actinoids (part of period 7

Element name	Symbol	Z	M	M^{3+}	RadiusM^{3+}/ pm
Actinium	Ac	89	*$[Rn]\ 6d^{1}7s^{2}$	$[Rn]5f^{0}$	111
Thorium	Th	90	*$[Rn\ ]5f\ 6d^{2}\ 7s^{2}$	$[Rn]5f^{1}$	
Protactinium	Pa	91	*$[Rn]5f^{2}6d^{1}7s^{2}$	$[Rn]5f^{2}$	
Uranium	U	92	*$[Rn]5f^{3}6d^{1}7s^{2}$	$[Rn]5f^{3}$	103
Neptunium	Np	93	*$[Rn]5f^{4}6d^{1}7s^{2}$	$[Rn]5f^{4}$	101
Plutonium	Pu	94	$[Rn]5f^{6}7s^{2}$	$[Rn]5f^{5}$	100
Americium	Am	95	$[Rn]5f^{7}7s^{2}$	$[Rn]5f^{6}$	99
Curium	Cm	96	*$[Rn]5f^{7}6d^{1}7s^{2}$	$[Rn]5f^{7}$	99
Berkelium	Bk	97	$[Rn]5f^{9}7s^{2}$	$[Rn]5f^{8}$	98
Californium	Cf	98	*$[Rn]5f^{10}7s^{2}$	$[Rn]5f^{9}$	98
Einsteinium	Es	99	$[Rn]5f^{11}7s^{2}$	$[Rn]5f^{10}$	
Fermium	Fm	100	$[Rn]5f^{12}7s^{2}$	$[Rn]5f^{11}$	
Mendelevium	Md	101	$[Rn]5f^{13}7s^{2}$	$[Rn]5f^{12}$	
Nobelium	No	102	$[Rn]5f^{14}7s^{2}$	$[Rn]5f^{13}$	
Lawrencium	Lr	103	$[Rn]5f^{14}6d^{1}7s^{2}$	$[Rn]5f^{14}$	

Or *$[Rn]5f^{9}6d^{1}7s^{2}$, *deviates from (n+l)

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LECTURE 2

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The uniqueness properties of **2^{nd} row elements** are due to

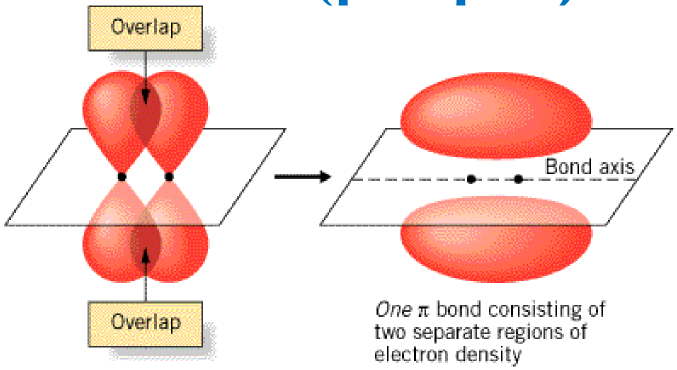
1 – Small size Small size leads to high IP, EA, and larger charge density e.g. F is most Electronegative than its group but EA of F is less than Cl , EA of O is less than S because adding e to these small atoms experience more e-e repulsion than larger atoms in their groups

high nuclear charge density Z*/r of Li, Be, B, C related to small size make covalent compounds of these elements because of high polarizing effect e.g. LiCl is more covalent because it polarizes the chloride anion cloud while NaCl is more ionic because Z*/r is lower and r Na^+> r Li^+ and hence polarizing effect of of Li cation is higher than that of Na cation

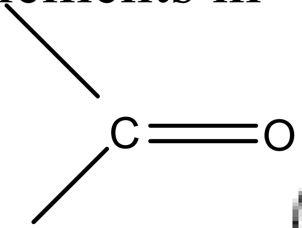
2- π (pi) bond formation

The small size of 2nd row elements increase the likelihood of π (pi) bond formation among them and with other elements in the form of **(p π-p π)**

-HC=CH- $N\equiv N$



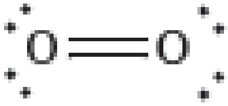
One π bond consisting of two separate regions of electron density



:N≡N:

(1.4)

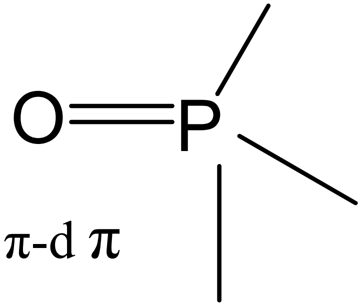
—C≡C—



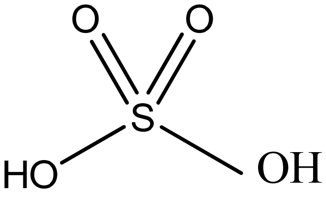
O=O

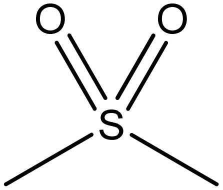
pπ- pπ

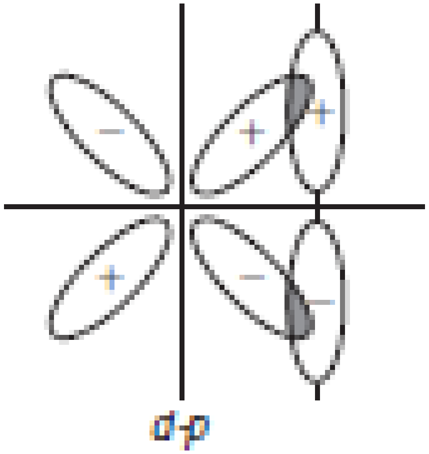
Or **p π-d π** with atoms containing empty d orbitals



Or p π-d π







dπ- pπ

3- The lack of *d* orbitals

It is an obvious fact that the elements Li to F are restricted to the set of 2*s* and 2*p* orbitals but their heavier congeners such as Na to Cl can use 3*s*, 3*p*, and 3*d* orbitals. This provides extra opportunities for bonding in the heavier elements that their lighter congeners do not enjoy. **2nd row elements have octet Lewis structure**

valency cannot have more than 4 bonds Maximum C.N=4(8e) or four electron pairs

the second row elements, Li to F, show a maximum covalence of 4, corresponding to a maximum hybridization of sp^3. In contrast, third row and heavier elements show 5, 6, and 7 coordination (Table 15.1) consistent with use of *d* orbitals.

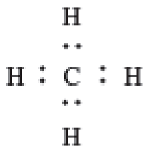


Table 15.1 Maximum Coordination Numbers of the Nonmetals

sp^3	CF_4 (4)	NF_3[a](3)	OF_2[a](2)	FF(1)	**electron pairs =4 octet rule,**
sp^3d^2	SiF_6^{-2} (6)	PF_6^-	SF_6	ClF_5 ⋮ IF_7 sp^3d^3 (7)	**High C.N=4,5,6,7 have empty d-oritals**

[a] N and O can achieve 4-coordination in onium salts, *e.g.*, NH_4^+.

Diagonal effect:

the top element in each group tends to resemble the second element of the group on the right in chemical and physical properties .

Elements of 2nd row differ in behavior from elements of their groups : Li is resembles Mg rather than its group Na → Cs , Be is closely related to Al than to its group ….etc (diagonal effect) here is related to resemblance in Z*/r of metals . Diagonal effect on non metals is related to resemblance in EN

Comparsion of f- elements with d- elements

The transition metal of d-block elements are d-partially filled shells (3d , 4d , 5d , 6d) . The d-orbital is projected well out to the periphery of the atoms and ions .

In marked contrast to this the (4f) orbitals in the lanthanoid elements are **rather deeply buried in the atom and ions**.

The behavior of actinides (5f) lies between the two types because the (5f) orbitals are **not so well shielded** as are the 4f orbitals although they are **not so exposed** as are the d-orbital elements

Lanthanoid contraction

There is a general **decrease** from left to right in the **radii** of main tr. metals as well as Lanthanoids this is called **Lanthanoid contraction**

The effective nuclear charge **Z***(?) experienced by 4f electrons **increases from left to right with increasing atomic numbers** , this is because the **shielding effect** of one (f) electron on the other from the effect of nuclear charge is **quite weak on account of the shapes of the f- orbitals.** **As a result** effective nuclear charge **Z*** **increases** and hence causes a **shrinkage in the radii** of atoms or ions as one proceeds from **La → Lu** which goes further to d-block of 2nd and third transition series.

Heavy metals and inert valence s^2 electron pair effect

The heavy metals of post transition metals of (period 6) (representative elements) located at at the end of groups :

	13	$({}_{81}\text{Tl})$	$[\text{Xe}]4f^{14}\,5d^{10}\,6s^{2}\,6p^{1}$
	14	$({}_{82}\text{Pb})$	$[\text{Xe}]4f^{14}\,5d^{10}\,6s^{2}6p^{2}$
	15	$({}_{83}\text{Bi})$	$[\text{Xe}]4f^{14}5d^{10}\,6s^{2}6p^{3}$
and	16	$({}_{84}\text{Po})$	$[\text{Xe}]4f^{14}\,5d^{10}6s^{2}6p^{4}$

are characterized of low activity of the electron pair of 6s orbitals of valence shell they are more stable when losing the p electrons only to form cations of valence lower than their groups by 2e and their compounds are more stable at

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LECTURE 3

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Oxidation states and oxidation number

***Elements farther to the right and higher up have high EN,EA, IP,Z* and smaller r (non metals) Assigned a (–) ox. States , so they intend to gain electron**

***Elements farther to the left and lower down, highly electropositive,**

High shielding effect, low EN,EA, IP & large r (metals)(they intend to lose electrons)Assigned (+) ox. states

(H = +1, -1)

Gr. IA (1) Li ⟶ Cs [N. g] ns^1 → +1 stable

Gr.IIA (2) Be ⟶ Ba [N. g] ns^2 → +2 stable

Gr.IIIA(13) B ⟶ Tl [N. g] ns^{2}np^1 → * (+1 , +3)

B Al Ga In *Tl

⟶

increased stability of +1, decreased stability of +3

Gr. IV A (14) [N.g] ns^2np^2

C	Si	Ge	Sn	Pb
+2, +4	+2, +4	+2, +4	+2, +4	+2, +4

$\longrightarrow$

Increased stability of (+2) , decreased stability of (+4)

Increased difficulty to lose ns^2 electron ($6s^2$)

Gr. VA(15) [N.g]ns^2np^3

N (−3) with metals

(+1, +2, +3, +4, +5) with nonmetals especially oxygen, and F e.g. NF_3 (+3)

P (−3) with metals

(+3, +5) with oxygen and halogens

As (−3 with IA , +3, +5 with oxygen and halogens)

Sb (+3, +5)

Bi (+3, +5)

P As Sb Bi

$\longrightarrow$

Increased stability of (+3)

Gr. VIA (16) [N.g] ns^2np^4

O (-2 , -1 , -½ , -⅓) with metals and low EN elements

(-2)	**oxide**	O^{2-}	
(-1)	**peroxide**	O_2^{2-}	
(-½)	**superoxide**	O_2^{-}	
(-⅓)	**ozonide**	O_3^{-}	
(+1 , +2)		F_2O , F_2O_2	**only with Fluorine**

S , Se , (−2, +4, +6)

Te −2 (unstable) , +4 , +6

Po (+4 , +6)

Gr. VIIA (17) [N.g] $ns^2\ np^5$ (Halogens)

F (-1) with metals & nonmetals

Cl , Br , I (-1) with metals & H

Ox. States +1 , +3 , +5 , +7 with F & oxygen

ClO^-, ClO_2^-, ClO_3^-, ClO_4^-

ClF

$$+3 \qquad +1 \qquad +7 \qquad +5$$

$$\xrightarrow{\hspace{6cm}}$$

Increased stability of ox. States

Gr. IIIA (18) [N.g] ns^2np^6 (noble gases)

He , Ne , Ar (Inert)

Kr Xe Rn

→

Increased reactivity with oxygen and F

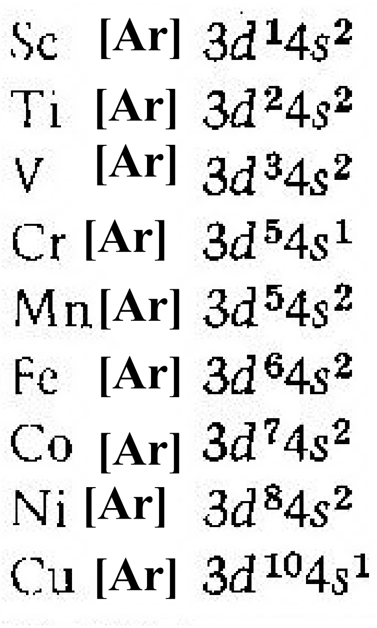
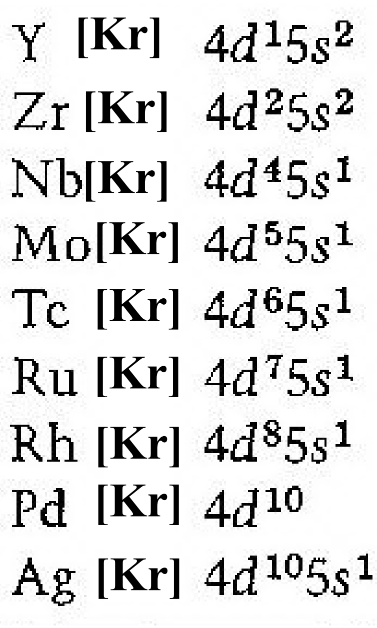
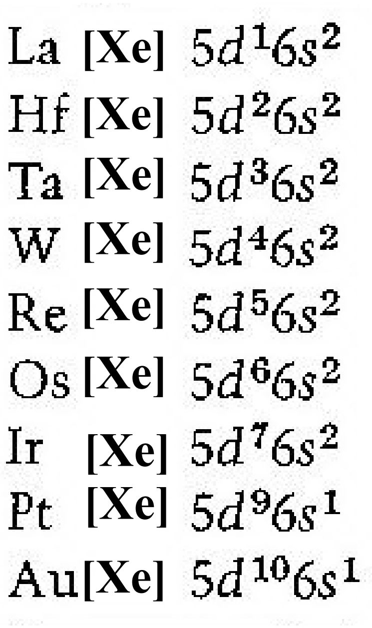
(+2) KrF_2 , XeF_2 , RnF_2

(+4) XeF_4 , (to a less degree $XeCl_4$)

(+6) XeF_6 , XeO_3

(+8) XeO_4 , XeO_6^{4-}

d- block elements with maximum oxidation state

(+3)	Sc	[Ar]	$3d^14s^2$	(+3)	Y	[Kr]	$4d^15s^2$	(+3)	La	[Xe]	$5d^16s^2$
(+4)	Ti	[Ar]	$3d^24s^2$	(+4)	Zr	[Kr]	$4d^25s^2$	(+4)	Hf	[Xe]	$5d^26s^2$
(+5)	V	[Ar]	$3d^34s^2$	(+5)	Nb	[Kr]	$4d^45s^1$	(+5)	Ta	[Xe]	$5d^36s^2$
(+6)	Cr	[Ar]	$3d^54s^1$	(+6)	Mo	[Kr]	$4d^55s^1$	(+6)	W	[Xe]	$5d^46s^2$
(+7)	Mn	[Ar]	$3d^54s^2$	(+7)	Tc	[Kr]	$4d^65s^1$	(+7)	Re	[Xe]	$5d^56s^2$
	Fe	[Ar]	$3d^64s^2$	(+8)	Ru	[Kr]	$4d^75s^1$	(+8)	Os	[Xe]	$5d^66s^2$
	Co	[Ar]	$3d^74s^2$		Rh	[Kr]	$4d^85s^1$		Ir	[Xe]	$5d^76s^2$
	Ni	[Ar]	$3d^84s^2$		Pd	[Kr]	$4d^{10}$		Pt	[Xe]	$5d^96s^1$
	Cu	[Ar]	$3d^{10}4s^1$		Ag	[Kr]	$4d^{10}5s^1$		Au	[Xe]	$5d^{10}6s^1$

Oxidation states of Lanthanoides

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
-	-	+2	-	+2	+2	-	-	-	-	-	+2	+2	-
+3	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3
+4	+4	+4					+4	+4					

Oxidation states of Actinoids

Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lw
									+2	+2	+ 2	+2	+2	
+3			+3	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3
	+4	+4	+4	+4	+4	+4	+4	+4	+4					
		+5	+5	+5	+5	+5								
			+6	+6	+6	+6								
				+7	+7									

The elements from Th →Np follow the behavior of Gr.4 → Gr.7 respectively of the main transition series by capability to lose all valence electrons and reach maximum oxidation state that correspond to [Rn] configuration then lower oxidation states become more stable especially (+3) from Am → Lr(w) similar to **lanthanoids** behavior

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LECTURE 4

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Oxides

Oxygen forms oxides by direct combination with all elements of periodic table (except the noble gases and noble metals Au, Pd, Pt).

The reaction is generally exothermic but some proceed slowly and requires heating to supply energy necessary to break the strong O=O bond. Then the reaction becomes exothermic

Classification of oxides

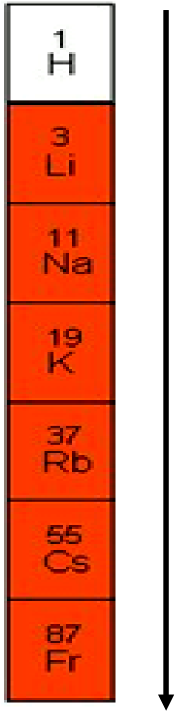
1- Classification of oxides according to ΔH_f^o & ΔG_f^o

Formation of oxides increase (or ΔH_f^o & ΔG_f^o increase) within a period from right to left

$\Delta G_f{}^\circ$ and Δ H_f^o decrease or heat evolved decrease down the group with increased atomic number (Z) of elements

H_f^o Li_2O = -72 K cal. / mol Δ

ΔH_f^o Na_2O = - 45 K cal. / mol .



Decrease of
ΔG° and Δ H_f^o
Of M_2O

2- Classification according to acidic & basic properties

A- Water soluble oxides

i- Acidic oxides

increase $[H_3O^+]$ when dissolved in H_2O

ii- Basic oxides

Increase pH when dissolved in H_2O

B – Water insoluble oxides

- i- Acidic oxides
- ii- Basic oxides
- iii- Amphoteric oxides

3- Classification according to bonding nature

i- Ionic oxides : IA , IIA oxides M_2O & MO , they crystallize in antifluorite structure , they exists in electrostatic attraction in the crystal lattice , they are basic in nature

ii- Covalent oxides : molecular oxides (acid anhydride) exist as gases , examples : oxides of light nonmetal s: F_2O , NO , SO_3 , SO_2 bond between oxygen and other atom is covalent in character . Most non metal oxides are acidic (P_4O_{10} , CO_2 N_2O_3) Some are neutral(NO, N_2O, halogen oxides, noble gases oxides)

iii- Oxides of metalloids and heavy nonmetals : They are solid with polymeric structure (SiO_2 , SnO_2 , GeO_2) or discrete molecules As_4O_{10} , P_4O_{10} , P_4O_6 , Sb_4O_6 , SeO_2 (polymer) TeO_2 (polymer)they with slightly basic or acidic properties

Oxides of heavy post transition metals of period 6 : The formula:

Gr	13	14	15	16	
	Tl_2O,	PbO ,	Bi_2O_3 ,	PoO_2	
	+1	+2	+3	+4	are stable Ox. state

←

Increased basicity

are more stable than the formula:

Tl_2O_3 ,	PbO_2 ,	Bi_2O_5 ,	PoO_3	
(unstable)		(oxidizing)		
+3	+4	+5	+6	Ox. state

←

Increased basicity

Increased stability of higher ox. State and their oxides increased and so their acidic property

FeO_4	not isolated
RuO_4	decomp.
OsO_4	isolated

decreased stability higher ox. State and their oxides

Increased stability of low oxidation state

Fe_2O_3	FeO	stable
Ru_2O_3	RuO	unstable
Os_2O_3	OsO	unstable

Inorganic Chemistry

Second year
1st semester

LECTURE 5

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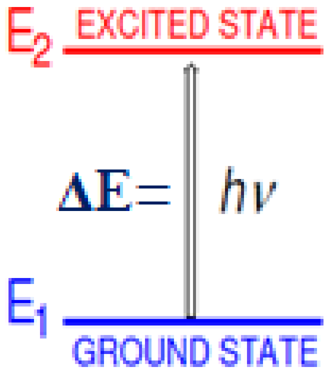
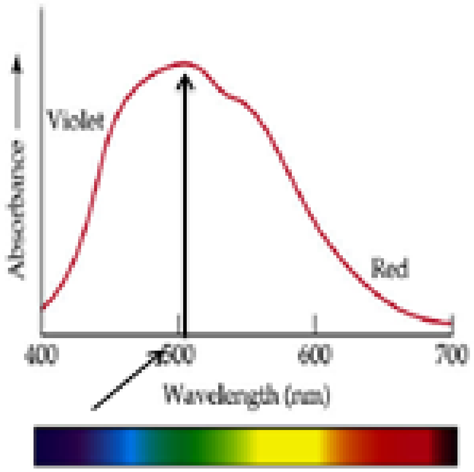
COLOURS OF INORGANIC COMPOUNDS

The color of any substance is related to the wavelength(s) of light absorbed by the substance.





The position of the band maximum, represents the energy gap ΔE

$(\Delta E) = h\upsilon = hc/\lambda$ $\qquad$ $\lambda = \dfrac{hc}{\Delta E}$

$\Delta E = hc\bar{v}$ ΔE(J/mole), h Plank's constant, λ wavelength(cm, nm, A°) , $\qquad$ **$\bar{v}$ wave number $\bar{v} = \dfrac{1}{\lambda}$ cm^{-1}**

The height of the absorption peak is given as the absorbance which varies greatly from one substance to another.
According to Beer-Lambert law The absorbance is defined as

$$\log_{10} I_o/I = A = \varepsilon.\ b.c$$

where **I_o** and **I** are intensity of light before and after passing through the absorbing medium respectively

A is the absorbance of the solutions as measured from the height of the absorption peak,
ε is the molar absorption coefficient (unit: L mol^{-1} cm^{-1}),
b is the optical path length of the sample (almost always equal to 1.00 cm), and
c is the molar concentration of the sample (M) .

Transition metal ions

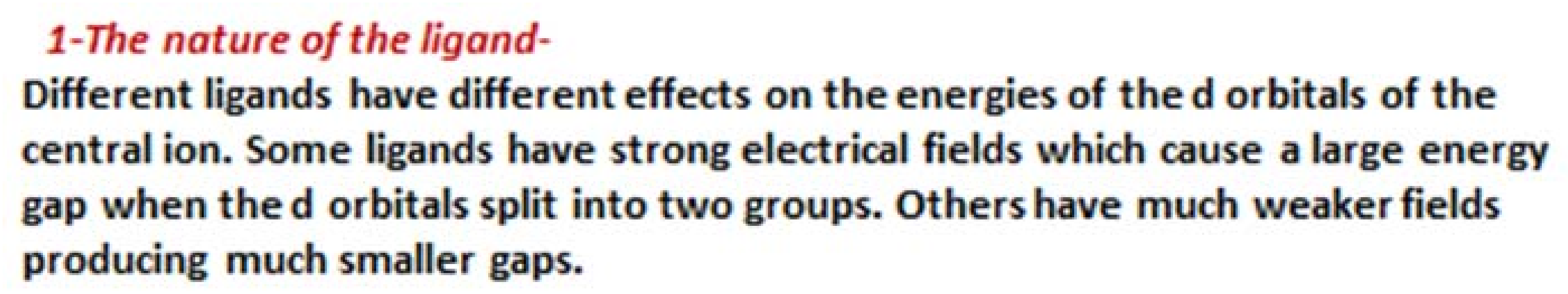
The transition metal complexes are coloured as they absorb wavelengths from visible light.The colors vary so much from ion to ion whereas most of non transition metal ions don't absorb visible light so they don't have colors.

That suggests that the partly filled d orbitals of transition metals must be involved in generating the color in some way.

Complexation of transition metal ions with the ligands cause the splitting of the five d- orbitals to low and high energy levels depending on the geometry of complex. The band gap ΔE between the two levels lies in the visible region.

The factors affecting the color (ΔE of absorption or splitting energy of d-orbitals) of transition metal complexes

1-The nature of the ligand
2-The oxidation state of the metal
3-The co-ordination of the ion
4-The nature of metal ion (Size of d-orbital , no. of unpaired electrons)

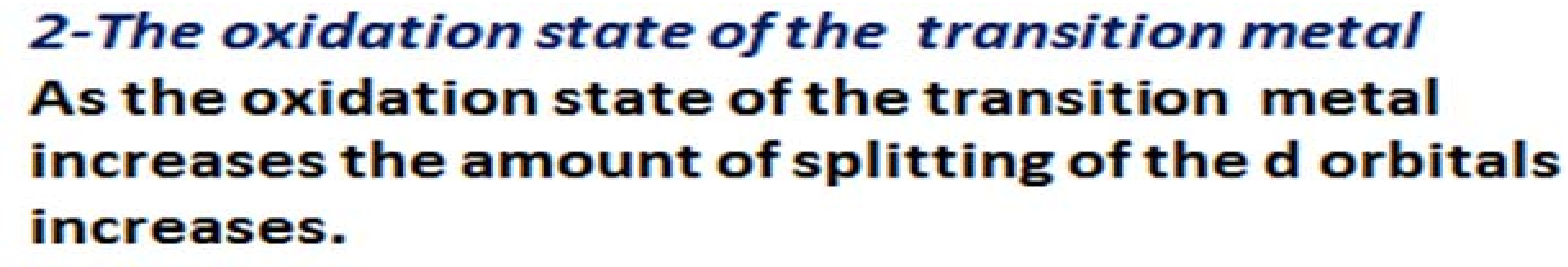


1-The nature of the ligand-

Different ligands have different effects on the energies of the d orbitals of the central ion. Some ligands have strong electrical fields which cause a large energy gap when the d orbitals split into two groups. Others have much weaker fields producing much smaller gaps.

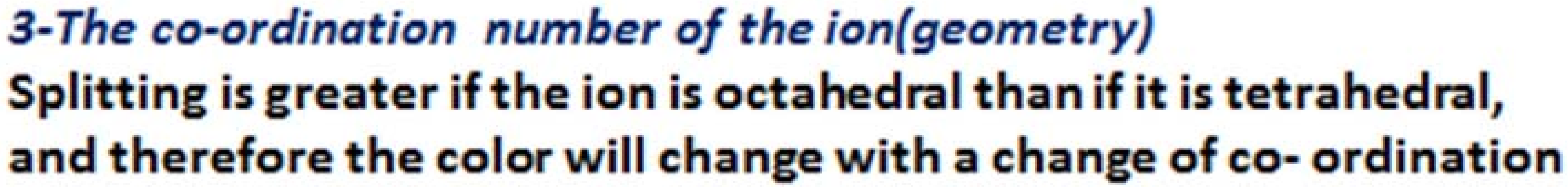
A spectrochemical series has been developed and sorted by the ability to split metal d-orbitals the stronger the ligand field the higher the splitting of d-orbitals

(Weakest) I^- < Br^- < S^{2-} < Cl- < SCN- < NO_3^- < N_3^- < F^- < OH^- < $C_2O_4^{2-}$ < H_2O< NCS^- < CH_3CN < py (pyridine) < NH_3 < en (ethylenediamine) <bipy (2,2'-bipyridine) < NO_2^- < PPh_3 < CN^- < CO(strongest)



2-The oxidation state of the transition metal

As the oxidation state of the transition metal increases the amount of splitting of the d orbitals increases.



3-The co-ordination number of the ion(geometry)

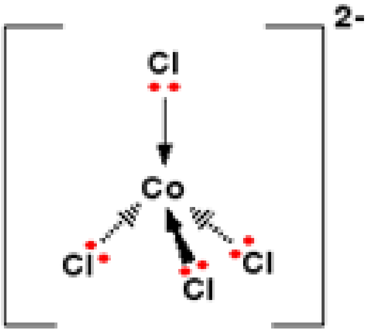
Splitting is greater if the ion is octahedral than if it is tetrahedral, and therefore the color will change with a change of co- ordination

4. *Size of the Metal Cation* –

For second and third-row transition metal ions, Δo is larger than that of first transition series. because of increased size of 4 and 5d -orbitals Less steric hindrance will occur between the ligands and better overlap between metal and ligand orbitals

Bonding in Complexes

$[CoCl_4]^{2-}$ **Tetrahedral Geometry**



$[Ni(CN)_4]^{2-}$ **Square Planar Geometry**

$[CoF_6]^{3-}$ **Octahedral sp^3d^2 Geometry**

$[Co(CN)_6]^{3-}$ **Octahedral d^2sp^3 Geometry**

Inorganic Chemistry

Second year
1st semester

LECTURE 6

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Magnetism

The magnetic moment resulting from *electron spin is denoted* μ_s *and* is called the **spin-only magnetic moment.**
The moment resulting from the electron *'orbiting' the nucleus is the* **orbital magnetic moment denoted** μ_L

The μ_s contributes most significantly to the observed magnetic moments, most particularly for first row transition metals.

S = n/2 = total spin quantum number, where *n equals the* number of unpaired electrons.

Magnetic Measurement

Experimental distinctiom *between* high-spin and low-spin complexes is based on the dertermination of their magnetic properties. Complexes are classified as diamagnetic if they tend to move out of magnetic field and paramagnetic if they tend to move into magnetic field. The higher the magnetic moment the greater the paramagnetism of the sample.

The spin-only paramagnetism μs which is characteristic of many d-metal complexes is obtained from the equation:

$$\boxed{\mu_s = g\,[S(S+1)]^{1/2} \quad = 2\,[S(S+1)]^{1/2}} \qquad \mu_B$$

g= gyromagnetic ratio = 2.003 and approximated to 2.0

μ_B is known as Bohr magneton

S: Total spin quantum number= n/2

Experimental values of magnetic moments are different from μ_s .o
this is because of orbital motion of the electron which also results in orbital contribution to the moment .

total magnetic moment = μ_L+S = $[4S(S+1)+L(L+1)]^{1/2}$

Magnetic Susceptibility

Magnetic moments are not measured directly but from magnetic susceptibility If a substance is placed in a magnetic field of magnitude Ho, the field produced within the substance is

$\Delta H = B - Ho$ B= induced field ΔH= field of substance

If $B < Ho$ $\Delta H(-)$ diamagnetism and If $B > Ho$ $\Delta H(+)$ paramagnetism

Molar susceptibility x_M = M wt. × x where x is specific mass susceptibility

Piere Curie established that:

x_M is inversely proportional with temperature

$x_M = C/T$ Curie law   C= Curie constant, T =temperature(K)

then the magnetic moment of the paramagnetic ion or molecule

$\mu_{eff} = 2.84[x_M T]^{1/2}$

Classifications of magnetic materials

Diamagnetism – *Results in a compound being* repelled by a magnetic field. Water and other compounds and ions having closed shells with paired electrons exhibit diamagnetism. , *diamagnetic* substances appear to **weigh slightly *less*** *in the presence of a magnetic* field. It is **not affected by temperature**.

Paramagnetism: A *property of compounds with one or more unpaired* electrons that results in a compound being drawn into a magnetic field. **Paramagnetism is much stronger than diamagnetism**, and a *paramagnetic substance that is drawn into the field appears to **weigh more** in the presence of a magnetic field.*

Classifications of magnetic materials (continued)

- **Ferromagnetism(Field and temp dependent)**
- Materials contain unpaired electrons in incomplete electron shells. **When placed in a magnetic field:**
- Magnetic moment of each atom is coupled to others in surrounding ‘domain” in such a way that they all become parallel and thus **reinforce each other**. The magnetic susceptibility of these materials is **inversely proportional with temperature**. There is a discontinuity at some Tc. Above Tc the substance becomes **paramagnetic and follows Curie law**

Classifications of magnetic materials(continued)

Anti-ferromagnetic materials

- Almost identical to ferromagnetic except that the moments of neighboring sub lattices are aligned opposite to each other and cancel out
- Thus **no net magnetization is measured**

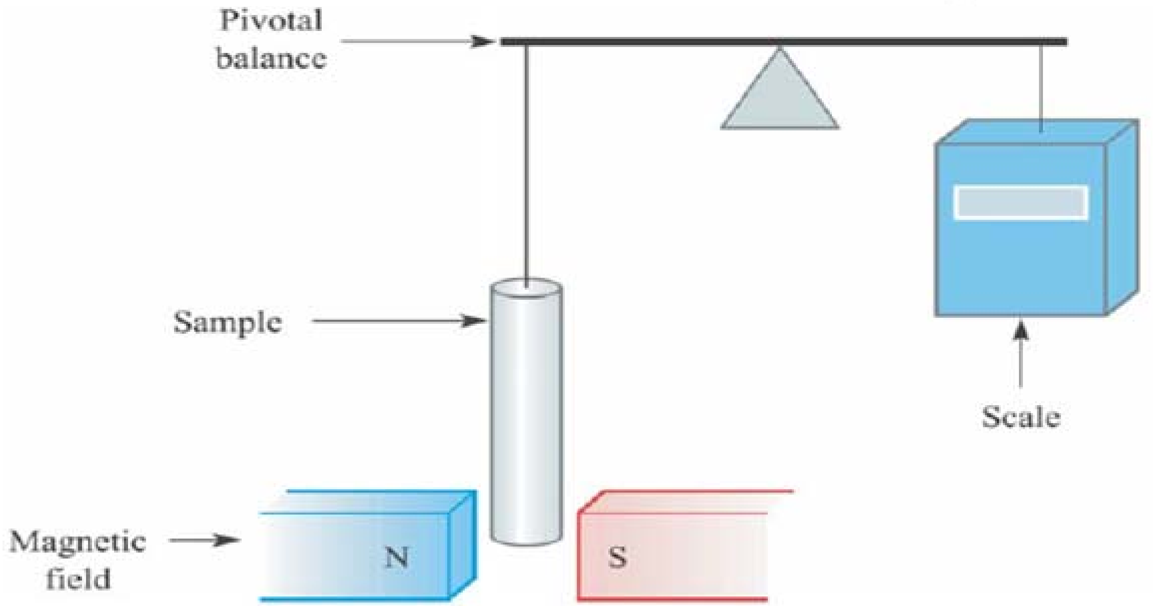
Example: Hematite Fe_2O_3, MnO, NiO, FeO.

Magnetism increases up to a temperature called **Neel temperature (T_N)** over which it becomes **paramagnetic** but below Neel temperature the susceptibility decrease with decreasing temperature

• Ferrimagnetic Materials

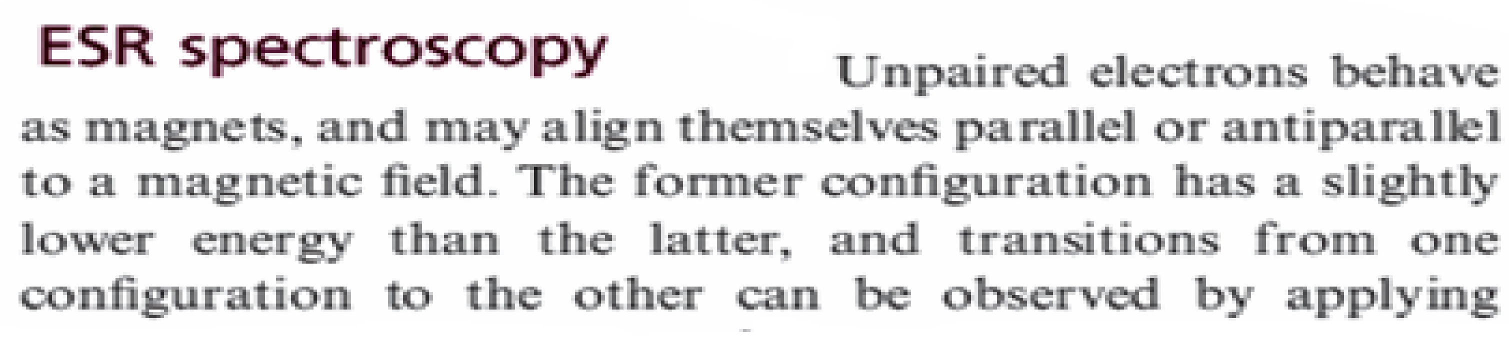
- Sublattices exhibit ferromagnetically but then couple antiferromagnetically between each other moments of opposite direction but different quantity
- Example: Magnetite Fe_3O_4

methods used to measure χ_m The Gouy method



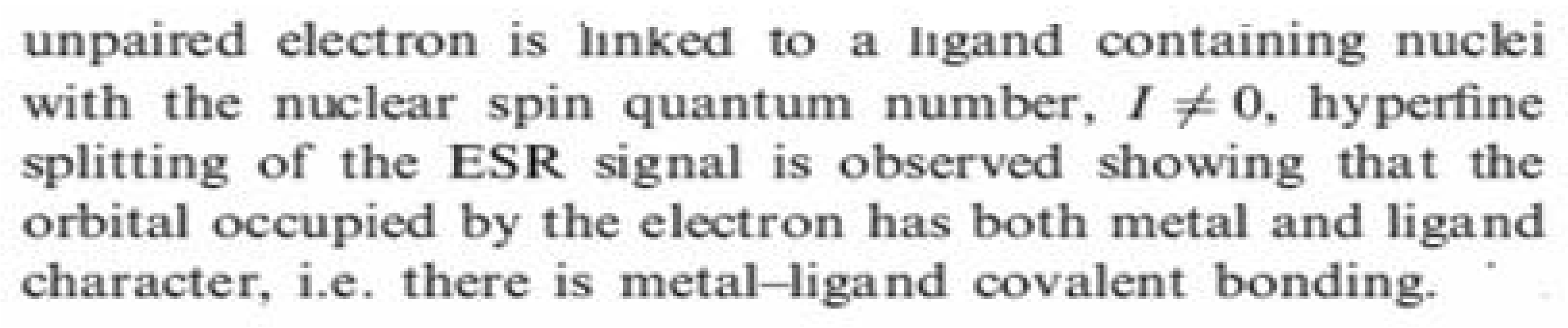
Schematic representation of Gouy balance

Initially the magnet is switched off, but upon applying a magnetic field, paramagnetic compounds are drawn into it by an amount that depends on the number of unpaired electrons. The change in weight caused by the movement of the sample into the field is recorded, and from the associated force it is possible to calculate the magnetic susceptibility of the compound. The effective magnetic moment is then derived using equation $\mu_{\text{eff}} = 2.828\sqrt{\chi_m T}$



ESR spectroscopy

Unpaired electrons behave as magnets, and may align themselves parallel or antiparallel to a magnetic field. The former configuration has a slightly lower energy than the latter, and transitions from one configuration to the other can be observed by applying microfrequency radiation . If the metal ion carrying unpaired electron is linked to a ligand containing nuclei with the nuclear spin quantum number, $I \neq 0$, hyperfine splitting of the ESR signal is observed showing that the orbital occupied by the electron has both metal and ligand character, i.e. there is metal–ligand covalent bonding.



EPR

EPR is the resonance absorption of microwave radiation by paramagnetic systems in the presence of an applied magnetic field

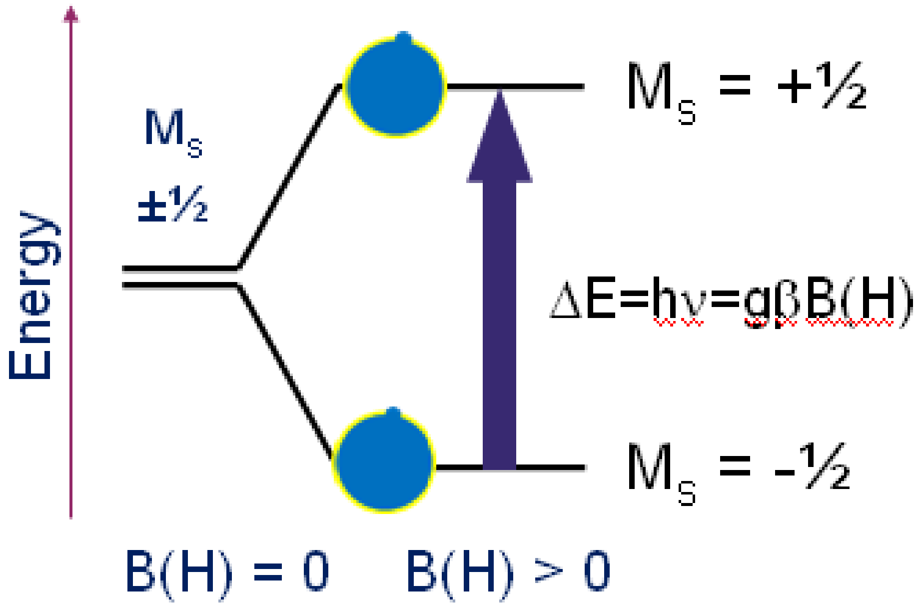
Electron Paramagnetic Resonance EPR)
Electron Spin Resonance (ESR)
Electron Magnetic Resonance (EMR)

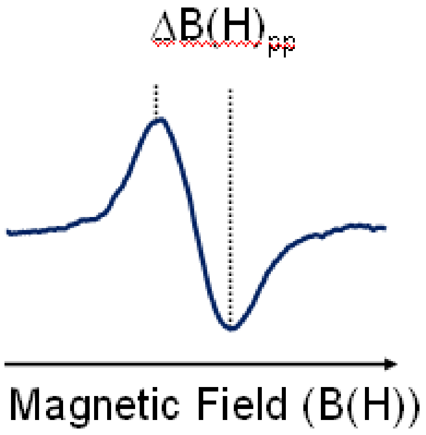
EPR ~ ESR ~ EMR

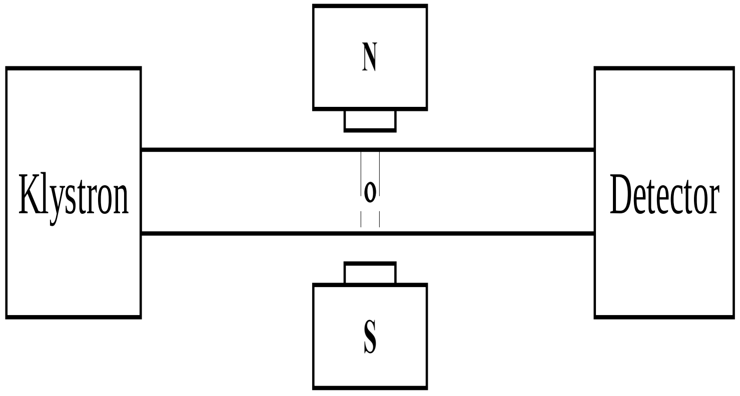
The energy difference between the two electron alignments

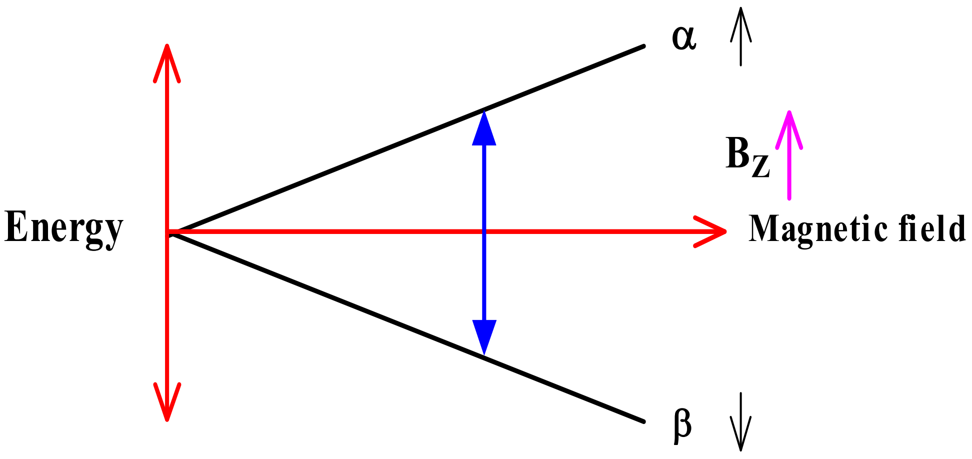
$$\boxed{\Delta E = h\upsilon = g\,.\mu_B\,.H}$$

h **Planck's constant 6.626196 x 10^{-27} erg.sec (or x 10^{-34} J.s)**
ν **frequency (MHz or GHz) for MW radiation 9000-36000MHz**
g **g-factor (approximately 2.0)**
μ_B **Bohr magneton (9.27401 x 10^{-24} JT^{-1} = 9.27401 x 10^{-28} JG^{-1}**
= 9.27401 x 10^{-21} erg.G^{-1}
(T=Tesla)= 10000 Gauss
B or (H) intensity of magnetic field (Gauss, G) 3300- 13000G= 0.33-1.3 Tesla


Energy
M_S
±½
M_S = +½
ΔE=hν=gβB(H)
M_S = -½
B(H) = 0
B(H) > 0


$\Delta B(H)_{pp}$
Magnetic Field (B(H))


N
Klystron
0
Detector
S


α
Energy
B_Z
Magnetic field
β

Inorganic Chemistry

Second year
1st semester

LECTURE 8

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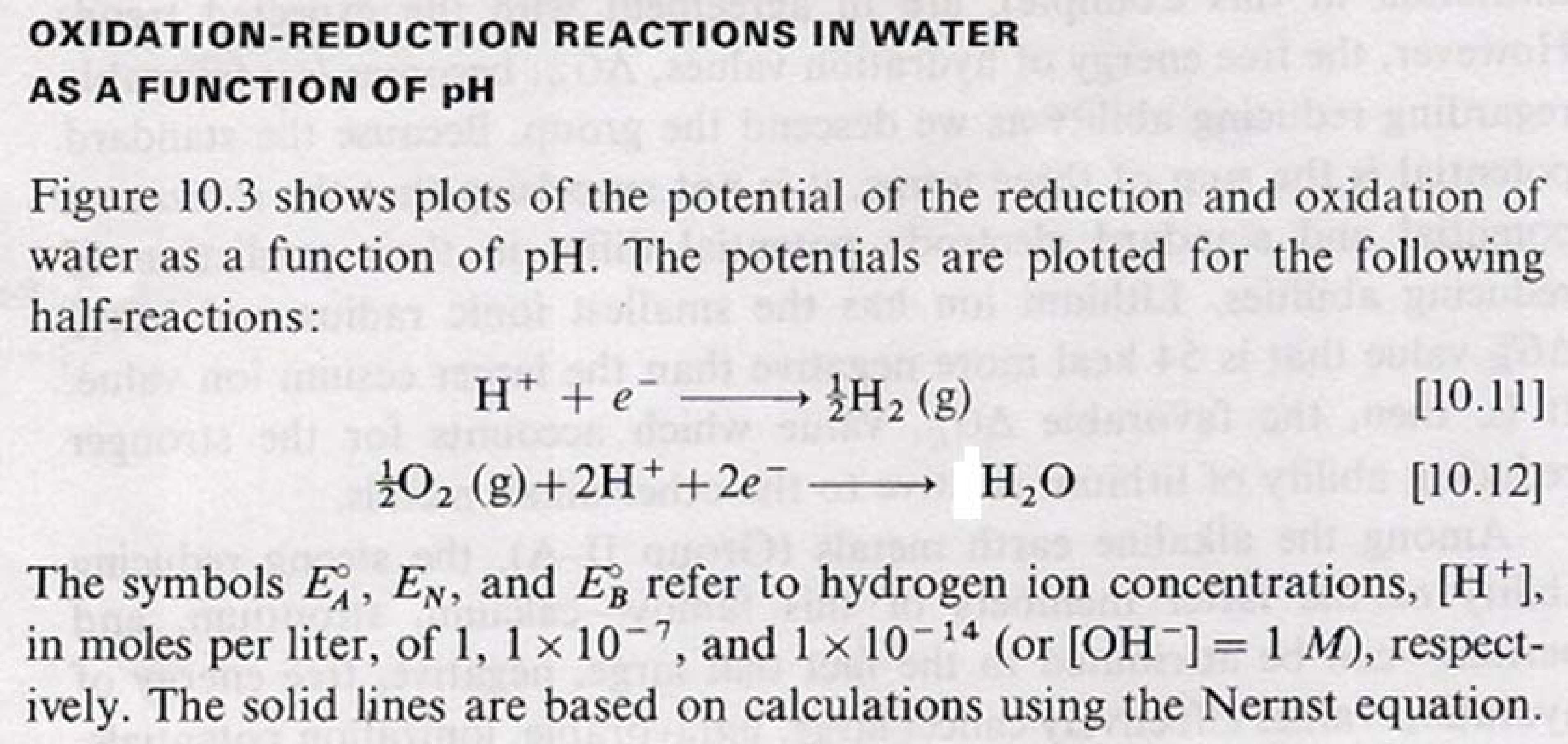
LECTURE 8

Electrochemistry
ELECTRODE POTENTIAL
PART 2



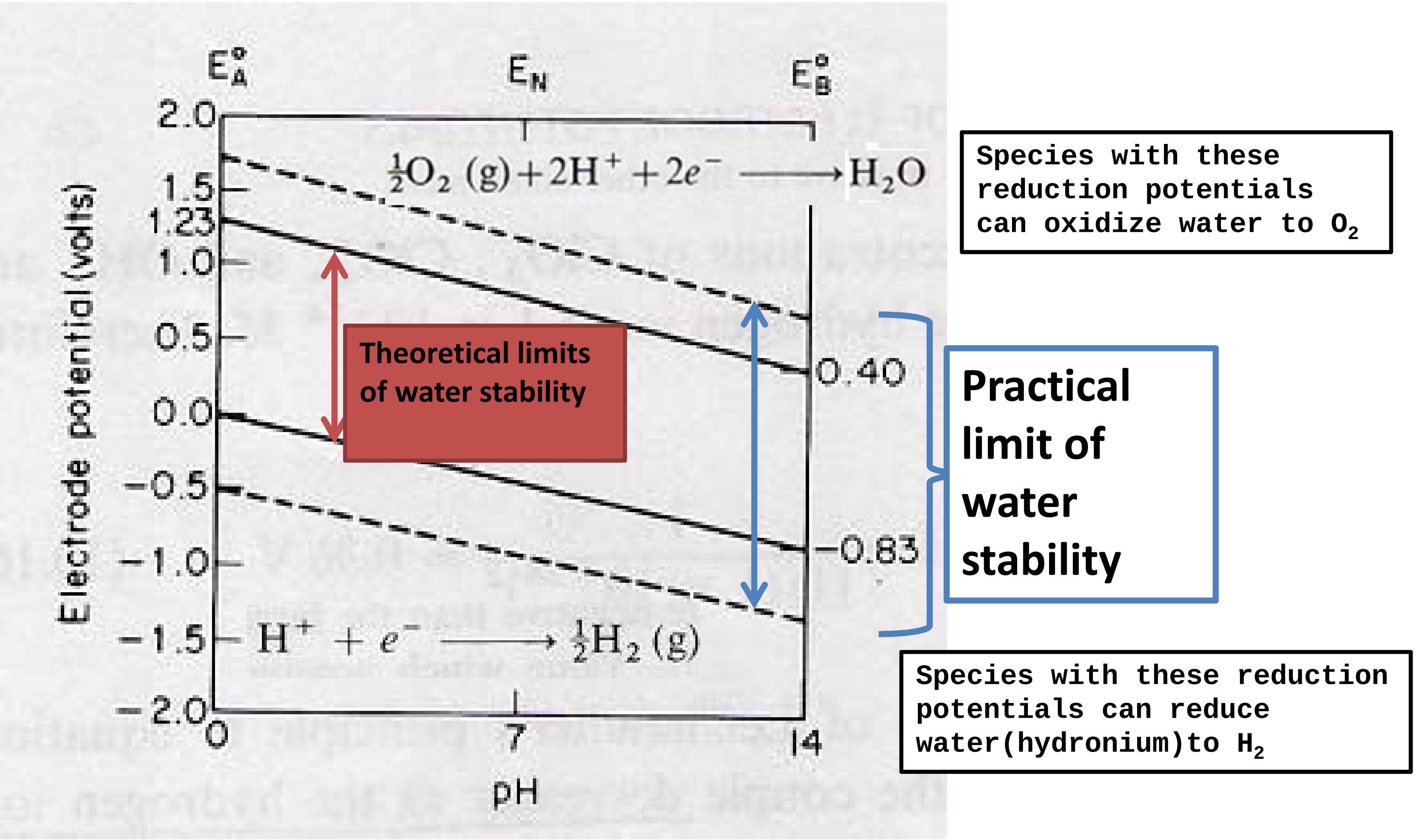
OXIDATION-REDUCTION REACTIONS IN WATER AS A FUNCTION OF pH

Figure 10.3 shows plots of the potential of the reduction and oxidation of water as a function of pH. The potentials are plotted for the following half-reactions:

$$H^+ + e^- \longrightarrow \tfrac{1}{2}H_2\,(g) \qquad [10.11]$$

$$\tfrac{1}{2}O_2\,(g) + 2H^+ + 2e^- \longrightarrow H_2O \qquad [10.12]$$

The symbols E_A°, E_N, and E_B° refer to hydrogen ion concentrations, $[H^+]$, in moles per liter, of 1, 1×10^{-7}, and 1×10^{-14} (or $[OH^-] = 1\ M$), respectively. The solid lines are based on calculations using the Nernst equation.



Species with these reduction potentials can oxidize water to O_2

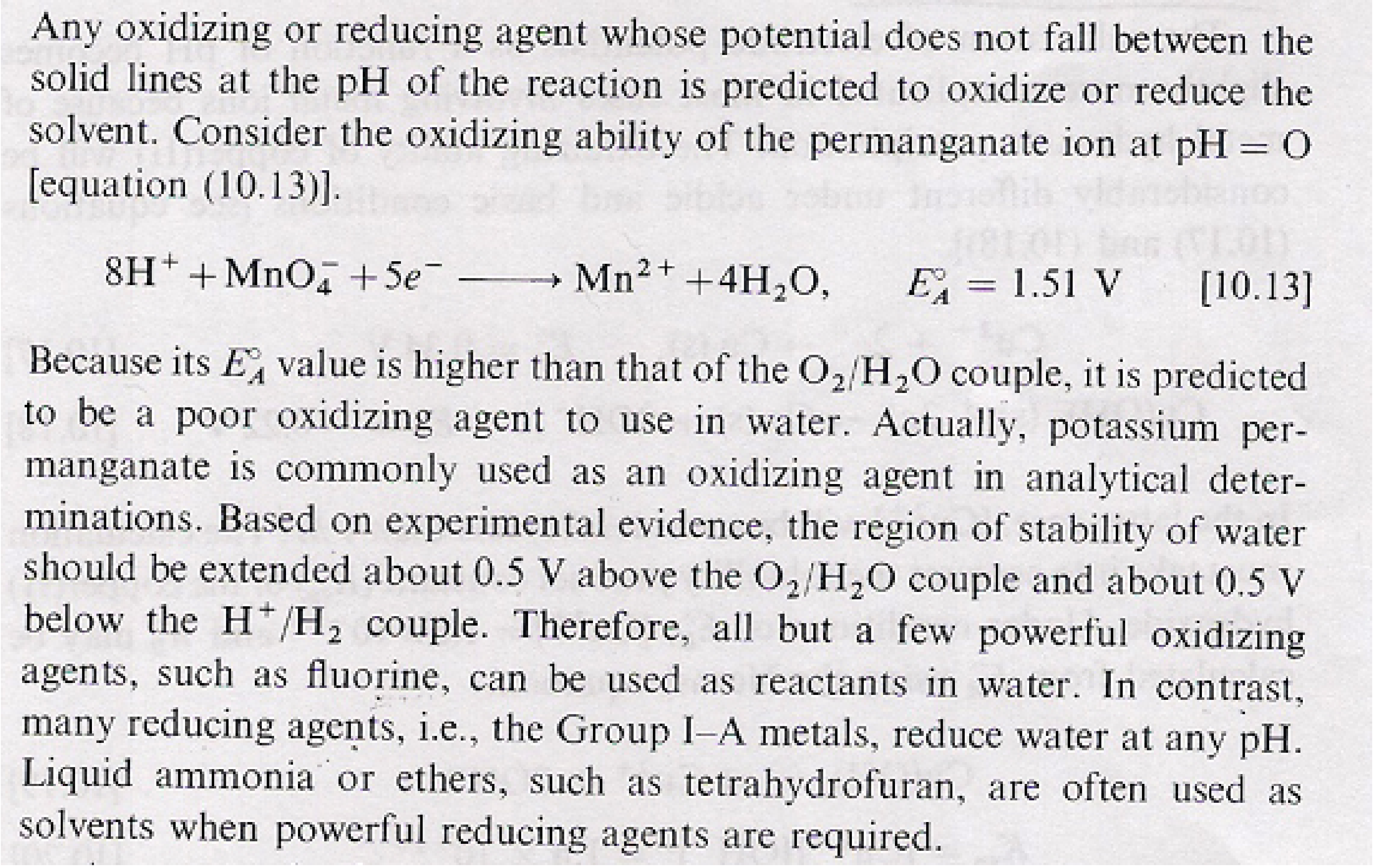
Theoretical limits of water stability

Practical limit of water stability

Species with these reduction potentials can reduce water(hydronium)to H_2

Figure 10.3 The electrode potential of the H^+ / H_2 and the O_2 / H_2O couples as function of PH

The solid lines are based on calculations using the Nernst equation



Any oxidizing or reducing agent whose potential does not fall between the solid lines at the pH of the reaction is predicted to oxidize or reduce the solvent. Consider the oxidizing ability of the permanganate ion at $\mathrm{pH} = \mathrm{O}$ [equation (10.13)].

$$8\mathrm{H}^+ + \mathrm{MnO}_4^- + 5e^- \longrightarrow \mathrm{Mn}^{2+} + 4\mathrm{H}_2\mathrm{O}, \qquad E_A^\circ = 1.51\ \mathrm{V} \qquad [10.13]$$

Because its E_A° value is higher than that of the $\mathrm{O}_2/\mathrm{H}_2\mathrm{O}$ couple, it is predicted to be a poor oxidizing agent to use in water. Actually, potassium permanganate is commonly used as an oxidizing agent in analytical determinations. Based on experimental evidence, the region of stability of water should be extended about 0.5 V above the $\mathrm{O}_2/\mathrm{H}_2\mathrm{O}$ couple and about 0.5 V below the $\mathrm{H}^+/\mathrm{H}_2$ couple. Therefore, all but a few powerful oxidizing agents, such as fluorine, can be used as reactants in water. In contrast, many reducing agents, i.e., the Group I–A metals, reduce water at any pH. Liquid ammonia or ethers, such as tetrahydrofuran, are often used as solvents when powerful reducing agents are required.

As suggested, whenever hydrogen ion or hydroxyl ion is involved in a reaction or half-reaction, the potential will be a function of pH and can be calculated using the Nernst equation. For example, for the reaction

$$2H^+ + ClO_4^- + 2e^- \rightarrow ClO_3^- + H_2O, \qquad E_A^\circ = 1.19\ \text{V} \qquad [10.14]$$

the appropriate expression of the Nernst equation is

$$E = E_A^\circ - \frac{0.0592}{2} \log \frac{[ClO_3^-]}{[ClO_4^-][H^+]^2} \qquad [10.15]$$

Under standard acidic conditions, all concentrations are unity, the log term is zero, and $E = E_A^\circ$. However, in determining the potential in basic solution, E_B°, from E_A°, the concentrations of ClO_3^-, ClO_4^-, and OH^- are unity but the concentration of the hydrogen ion is 1×10^{-14} *M*. Therefore, the Nernst equation is

$$E_B^\circ = 1.19 - \frac{0.0592}{2} \log \frac{1}{(1)(1 \times 10^{-14})^2} = 0.36\ \text{V} \qquad [10.16]$$

The calculation of electrode potentials as a function of pH becomes slightly more complicated in most cases involving metal ions because of metal hydroxide precipitation. The oxidizing ability of copper(II) will be considerably different under acidic and basic conditions [see equations (10.17) and (10.18)].

$$Cu^{2+} + 2e^- \rightarrow Cu\,(s), \qquad E^\circ_A = 0.34\ \text{V} \qquad [10.17]$$

$$Cu(OH)_2\,(s) + 2e^- \rightarrow Cu\,(s) + 2OH^-, \qquad E^\circ_B = -0.22\ \text{V} \qquad [10.18]$$

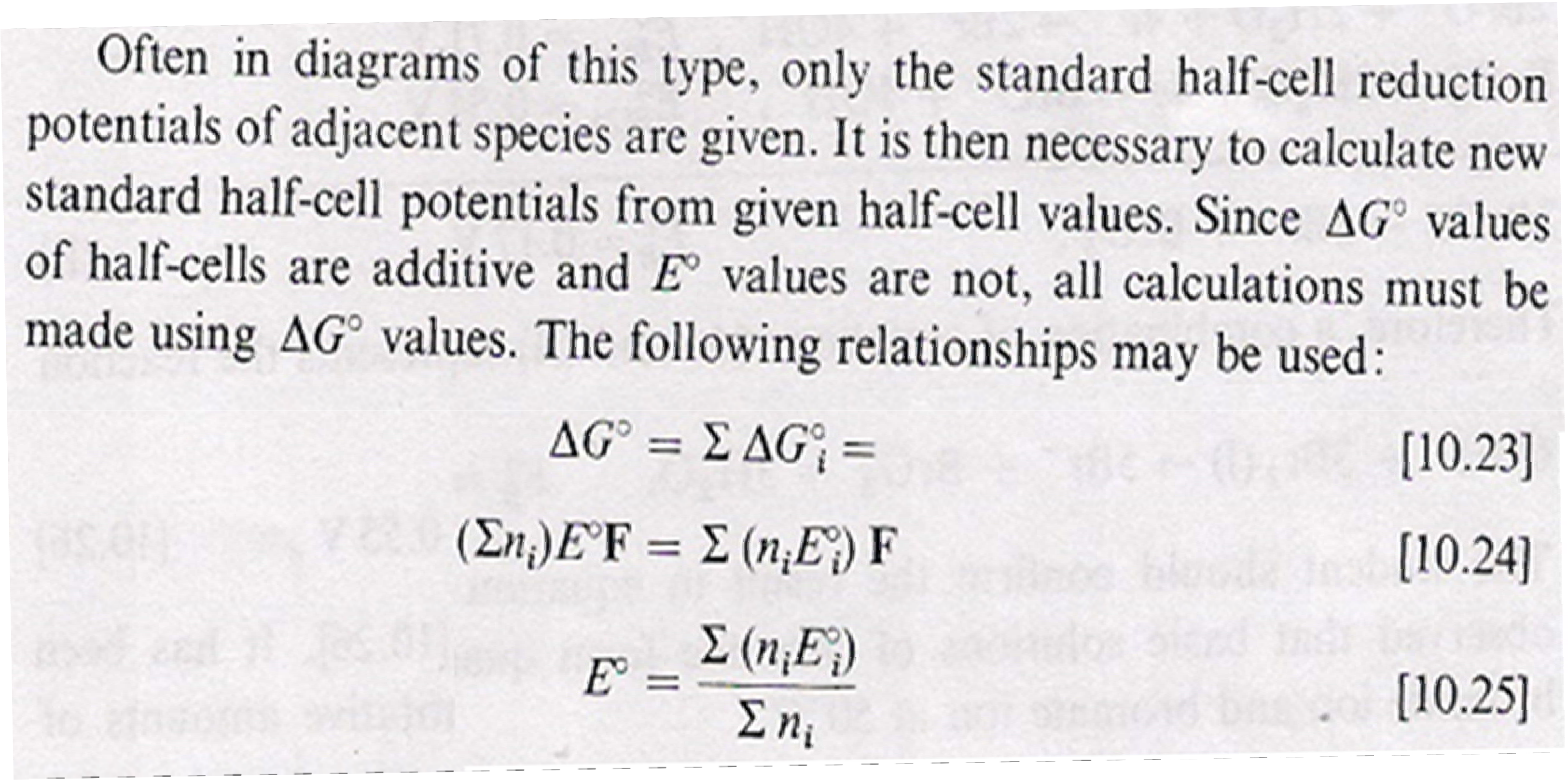
In the latter case, $[Cu^{2+}]$ will be considerably less than 1 M. The calculation must take into account the solubility product constant (K_{sp}) of the copper(II) hydroxide. Under conditions of E°_B, $[Cu^{2+}] = 1.6 \times 10^{-19}$ and E°_B may be calculated from E°_A using the Nernst equation.

$$Cu(OH)_2\,(s) \rightleftarrows Cu^{2+} + 2OH^- \qquad [10.19]$$

$$K_{sp} = [Cu^{2+}][OH^-]^2 = 1.6 \times 10^{-19} \qquad [10.20]$$

$$E^\circ_B = 0.34 - \frac{0.0592}{2}\log\frac{1}{1.6 \times 10^{-19}} = -0.22\ \text{V} \qquad [10.21]$$

Electromotive force diagrams-Latimer diagram



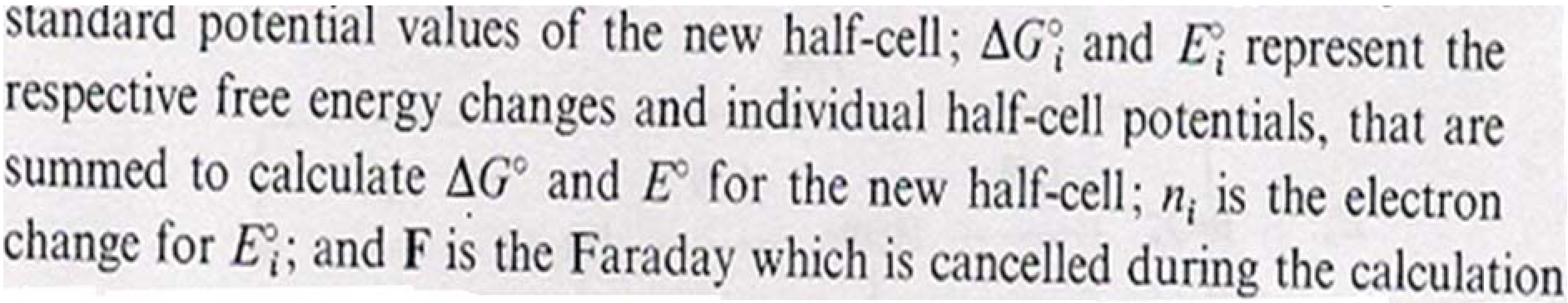
Often in diagrams of this type, only the standard half-cell reduction potentials of adjacent species are given. It is then necessary to calculate new standard half-cell potentials from given half-cell values. Since ΔG° values of half-cells are additive and E° values are not, all calculations must be made using ΔG° values. The following relationships may be used:

$$\Delta G^\circ = \Sigma\, \Delta G^\circ_i = \qquad [10.23]$$

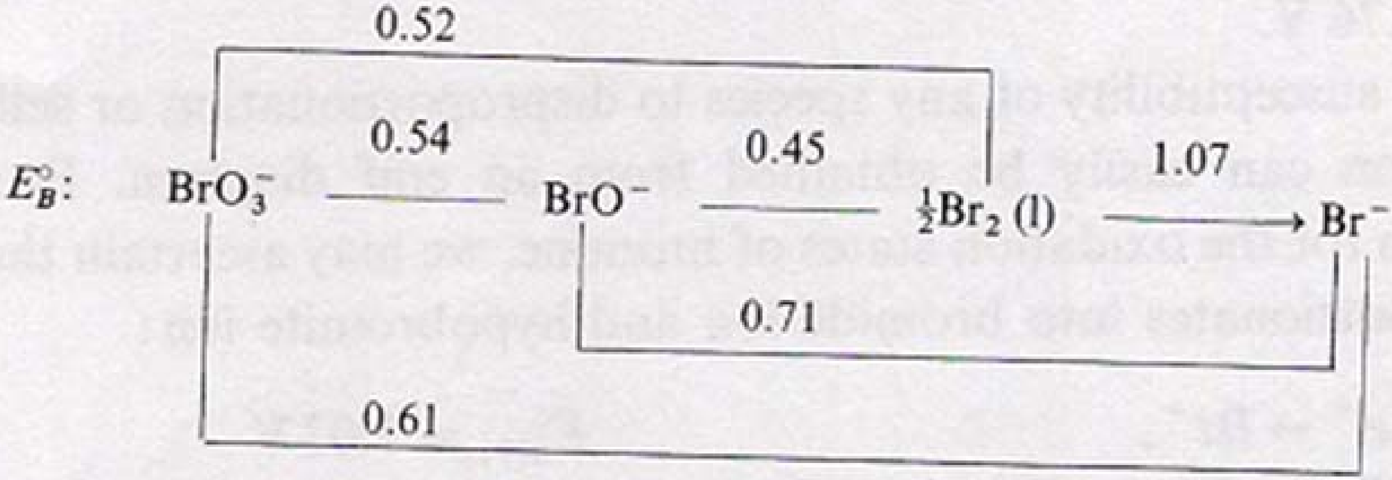
$$(\Sigma n_i) E^\circ \mathrm{F} = \Sigma\, (n_i E^\circ_i)\, \mathrm{F} \qquad [10.24]$$

$$E^\circ = \frac{\Sigma\, (n_i E^\circ_i)}{\Sigma\, n_i} \qquad [10.25]$$

ΔGº and Eº represent the free energy change and

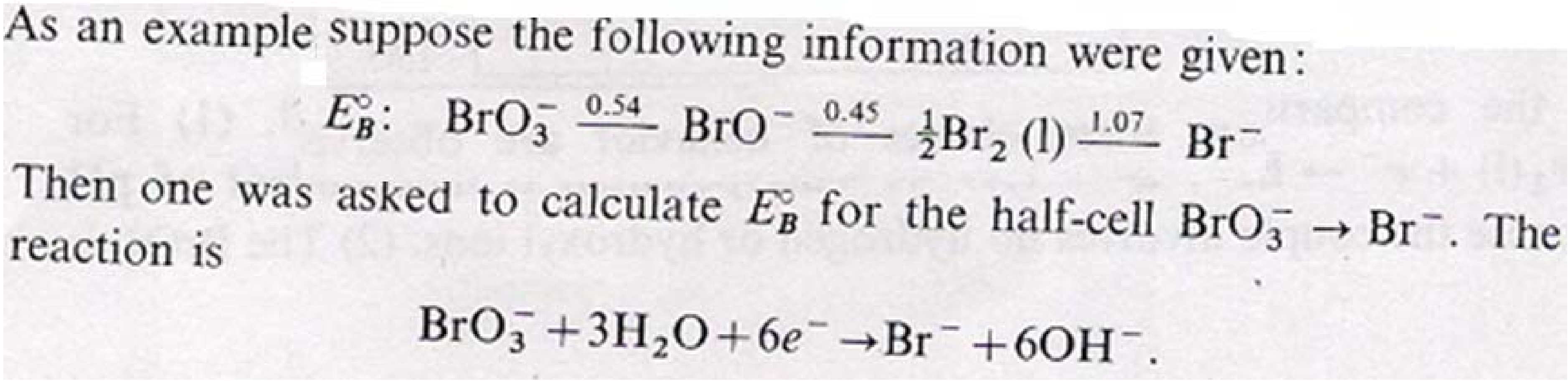


standard potential values of the new half-cell; ΔG°_i and E°_i represent the respective free energy changes and individual half-cell potentials, that are summed to calculate ΔG° and E° for the new half-cell; n_i is the electron change for E°_i; and **F** is the Faraday which is cancelled during the calculation bromine in basic solution; E_B° represents standard conditions at which hydroxyl ion concentration is 1 M.



The diagram abbreviates the half-reactions, and the signs of the potential designate the direction of the reaction corresponding to standard half-cell reduction potentials; for example, $BrO_3^- \xrightarrow{0.54} BrO^-$ is an abbreviation of the following half reaction:

$$BrO_3^- + 2H_2O + 4e^- \rightarrow BrO^- + 4OH^-, \qquad E_B^\circ = 0.54 \text{ V} \qquad [10.22]$$



As an example suppose the following information were given:

$$E_B^\circ:\quad BrO_3^- \xrightarrow{0.54} BrO^- \xrightarrow{0.45} \tfrac{1}{2}Br_2\,(l) \xrightarrow{1.07} Br^-$$

Then one was asked to calculate E_B° for the half-cell $BrO_3^- \rightarrow Br^-$. The reaction is

$$BrO_3^- + 3H_2O + 6e^- \rightarrow Br^- + 6OH^-.$$

$BrO_3^- + 4e + 2H_2O \rightarrow BrO^- + 4OH^-$ $\quad E^\circ = +0.54$ V

$BrO^- + e + H_2O \rightarrow \tfrac{1}{2} Br_{2\,(l)} + 2OH^-$ $\quad E^\circ = +0.45$ V

$\tfrac{1}{2} Br_2(l) + e \rightarrow Br^-$ $\quad E^\circ = 1.07$ V

$BrO_3^- + 6e + 3H_2O \rightarrow 6OH^- + Br^-$

$$E^\circ = \frac{0.54x\ 4 + 0.45x1 + 1.07x1}{6} = 0.61\ \text{V}$$

For the reaction diagram $\quad BrO_3^- \rightarrow \tfrac{1}{2} Br_{2\,(l)}$

$BrO_3^- + 5e + 3H_2O \rightarrow 6OH^- + \tfrac{1}{2} Br_{2\,(l)}$

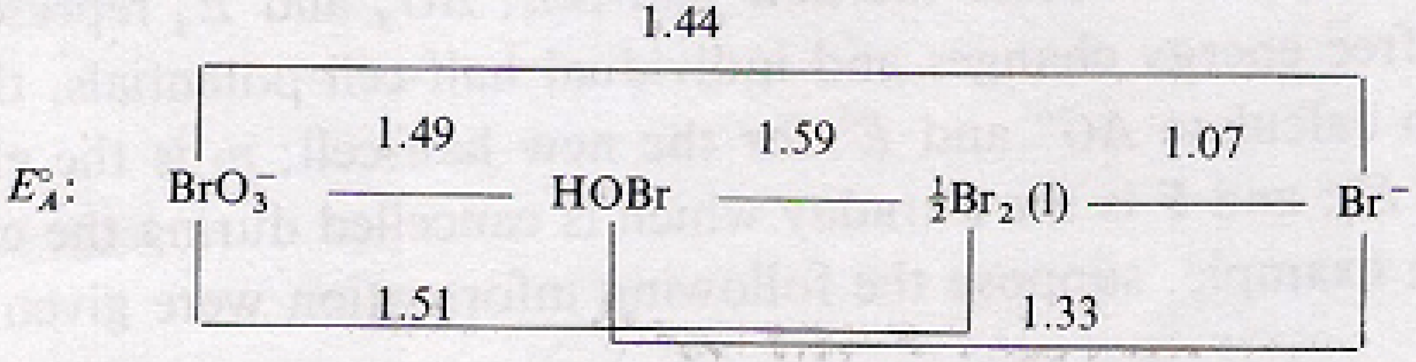
$$E^\circ = \frac{0.54x\ 4 + 0.45x1}{5} = 0.522\ \text{V}$$

DISPRORTIONATION :

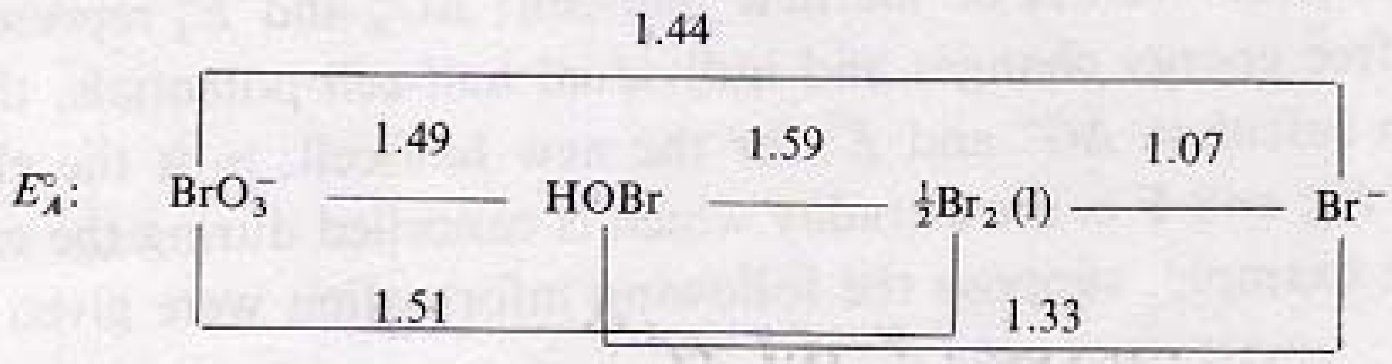
Stability of species at different media :

Disproportionation or self oxidation – reduction of a species occur When the value of E° on the right of the species is higher than the value on the left in the Latimer diagram

It is instructive to compare the emf diagram for bromine in acidic solution ($[H^+] = 1\ M$), E_A°, with that of the E_B° diagram.



In the comparison, three classes of behavior are observed. (1) For $\frac{1}{2}Br_2(l) + e^- \rightarrow Br^-$, $E^\circ = 1.07$ V. This potential is independent of pH because the couple involves no hydrogen or hydroxyl ions. (2) The BrO_3^- is a better oxidizing agent (more easily reduced) in an acidic solution than in a basic solution. (3) The potential changes as a function of pH when the nature of one or more of the species in the couple is pH dependent. For example, HOBr, a weak acid, exists in its molecular and ionized forms in acidic and basic solutions, respectively.

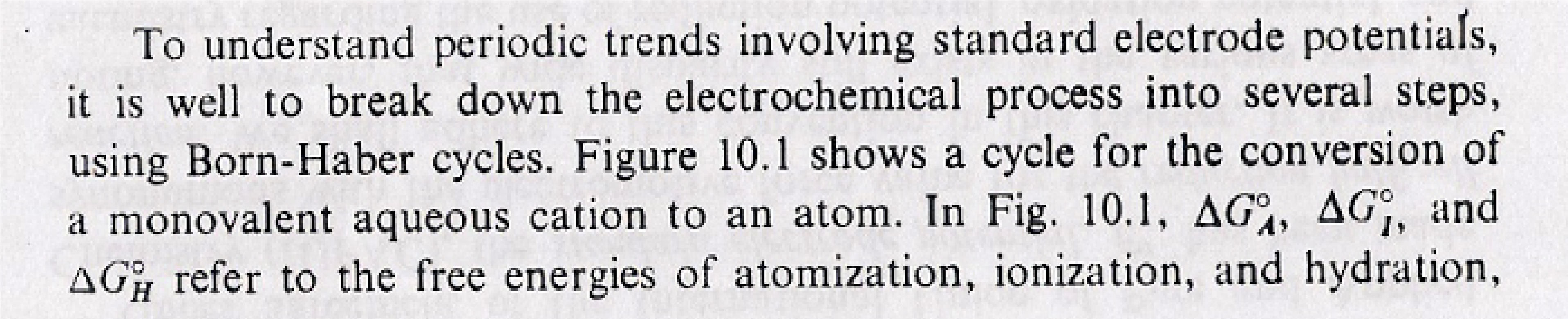


From the E_A° diagram for bromine, we see that it will not disproportionate in acidic solution to Br^- and HOBr ($E_A^\circ = 1.07 - 1.59 = -0.52$ V) or to Br^- and BrO_3^- ($E_A^\circ = 1.07 - 1.51 = -0.44$ V). This contrast in behavior in the two solutions, acidic and basic, occurs because the oxidizing ability of Br_2 is independent of pH. However, from the acidic medium diagram for bromine, it can be predicted that HOBr disproportionates into BrO_3^- and Br_2 [equation (10.27)].

$$5HOBr \rightarrow 2Br_2\,(l) + BrO_3^- + H^+ + H_2O, \qquad E_A^\circ = 0.10\text{ V} \qquad [10.27]$$

However, E_A° for reaction [10.27] is very near zero, and it is not surprising that some HOBr exists in solution.

Periodic Trend For E^o Using Born –Harber Cycle



To understand periodic trends involving standard electrode potentials, it is well to break down the electrochemical process into several steps, using Born-Haber cycles. Figure 10.1 shows a cycle for the conversion of a monovalent aqueous cation to an atom. In Fig. 10.1, ΔG°_A, ΔG°_I, and ΔG°_H refer to the free energies of atomization, ionization, and hydration,

Conversion of M^+_{aq} to $M_{(S)}$ $(M^+_{aq}/M_{(s)})$

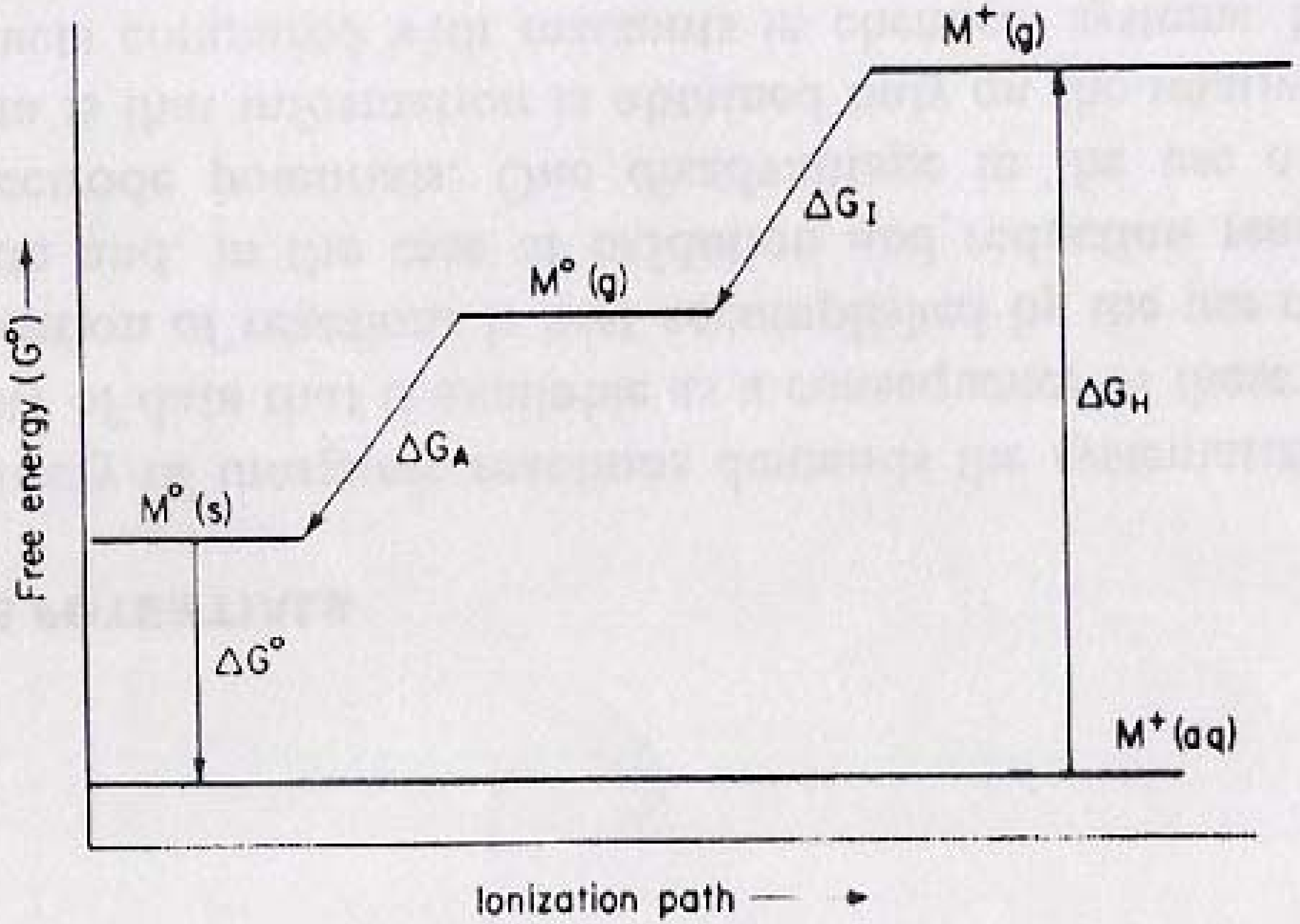


Figure 10.1. Born-Haber cycle showing energy contributions for the reduction of an aqueous cation to the metal.

Periodic Trend For E^o Using Born –Harber Cycle

1-Metals

1-ΔG^o of atomization(sublimation) $\Delta G^o_{A(s)}$ (+) endothermic

$M(s) \rightarrow M(g) \qquad \Delta G^o_A$ (+)

2- ΔG^o_{IP} (ionization potential) (+)

$M(g) \rightarrow M^+(g) + e \qquad \Delta G^o_{IP}$ (+)

3- $\Delta G^o_{(h)}$ (-) (highly exothermic)

$M^+(g) + nH_2O \rightarrow M^+_{(aq)} \qquad \Delta G^o_{(h)}$ (-)

$$\Delta G^{o} M(s)/M^{+}(aq) = \Delta G^{o}{}_{A} + \Delta G^{o}{}_{IP} + \Delta G^{o}{}_{(h)}$$

$$\Delta G^{o}\ M^{+}(aq)/M(s) = -\Delta G^{o}{}_{A}(+) - \Delta G^{o}{}_{IP}(+) - \Delta G^{o}{}_{(h)}(-)$$

$$\Delta G^{o}\ Li^{+}(aq)/Li(s) = -30.6 - 125 + 122 = -30.4\ \text{Kcal/mole}$$

Conversion of a halogen to a halide ion (½ X_2 / X^-)

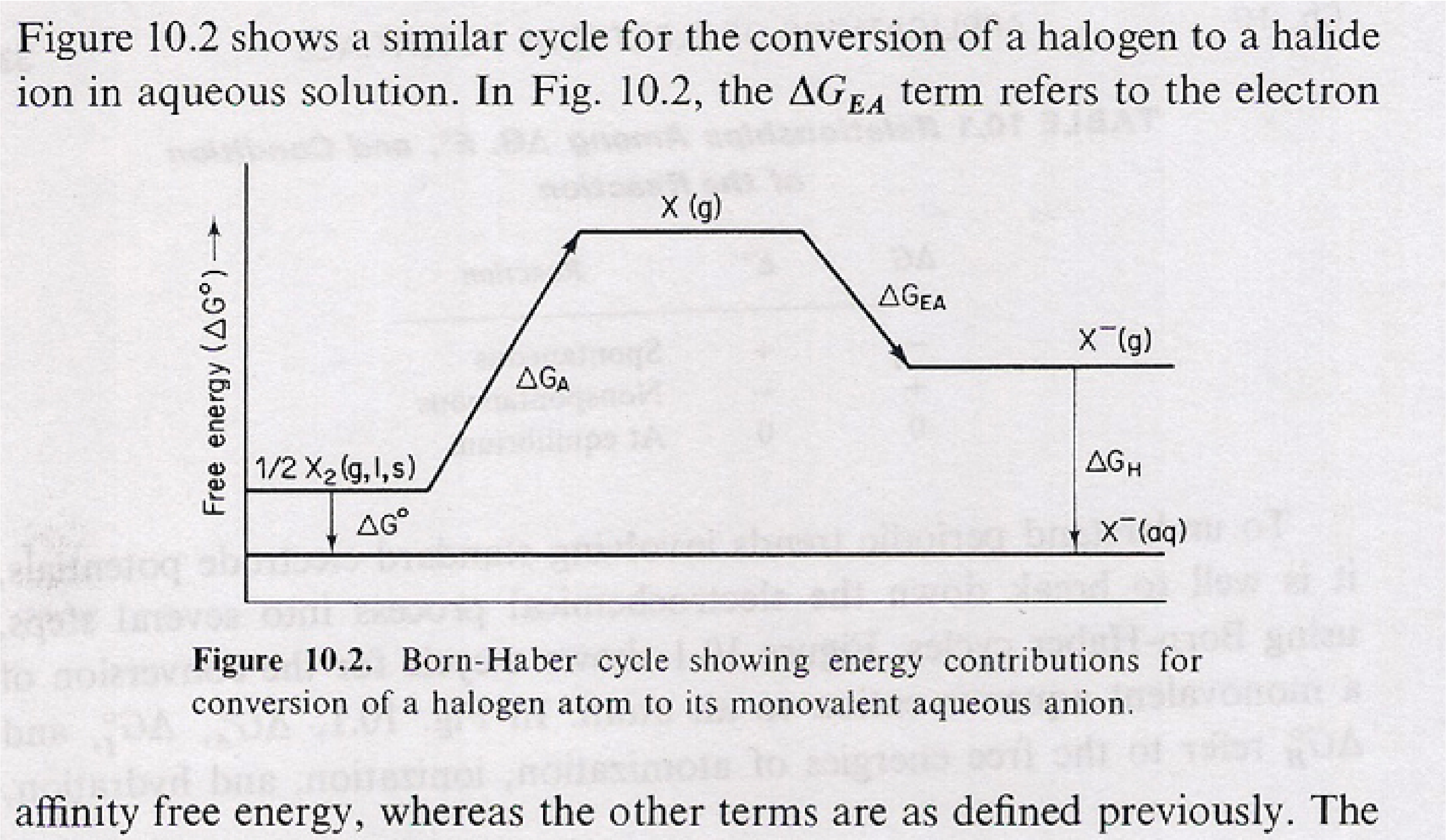


Figure 10.2 shows a similar cycle for the conversion of a halogen to a halide ion in aqueous solution. In Fig. 10.2, the ΔG_{EA} term refers to the electron

Figure 10.2. Born-Haber cycle showing energy contributions for conversion of a halogen atom to its monovalent aqueous anion.

affinity free energy, whereas the other terms are as defined previously. The equation relating these terms is

$$\Delta G^\circ = \Delta G^\circ_A + \Delta G^\circ_{EA} + \Delta G^\circ_H \qquad [10.7]$$

The ΔG°_H term plays a less significant role here than in the ionization of a metal. This is not unexpected, considering the lower hydration energies of the larger anions compared with those of smaller cations.

2-Non Metals(e.g.Halogens)

1-ΔG^o of atomization or sublimation (dissociation energy) $\Delta G^o_A(s)$ endothermic (+)

$\frac{1}{2} X_2(g) \rightarrow X(g)$ ΔG^o_A (+)

2- ΔG^o_{EA} (electron affinity) (exothermic) (-)

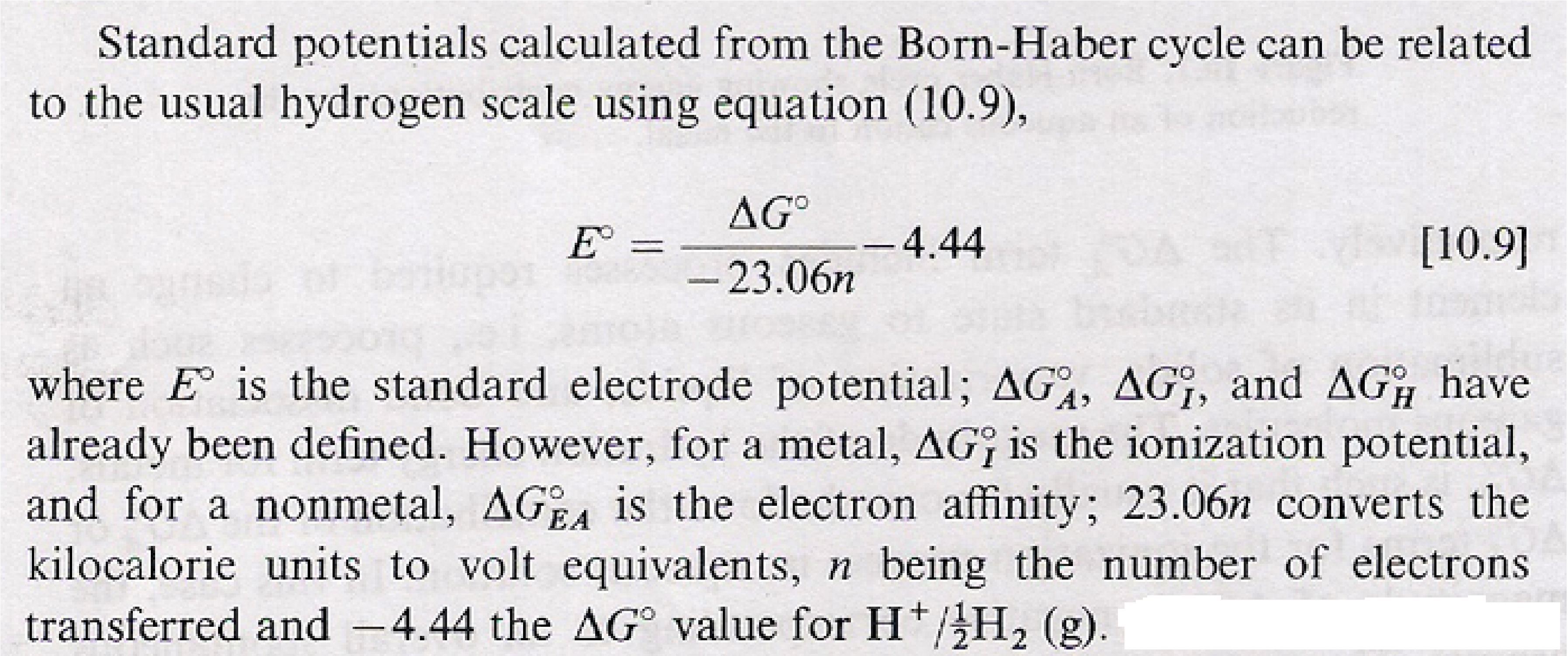
$X(g) + e \rightarrow X^-(g)$ ΔG^o_{EA} (-)

3- $\Delta G^o_{(h)}$ (exothermic)(-)

$X^-(g) + nH_2O \rightarrow X^-_{(aq)}$ $\Delta G^o_{(h)}$ (-)

$\Delta G^o_{\frac{1}{2} X2(g) / X^-(g)} = \Delta G^o_A + \Delta G^o_{EA} + \Delta G^o_{(h)}$

$\Delta G^o_{\frac{1}{2} X2(g) / X^-(g)} = \Delta G^o_A(+) + \Delta G^o_{EA}(-) + \Delta G^o_{(h)}(-)$



Standard potentials calculated from the Born-Haber cycle can be related to the usual hydrogen scale using equation (10.9),

$$E^\circ = \frac{\Delta G^\circ}{-23.06n} - 4.44 \qquad [10.9]$$

where E° is the standard electrode potential; ΔG°_A, ΔG°_I, and ΔG°_H have already been defined. However, for a metal, ΔG°_I is the ionization potential, and for a nonmetal, ΔG°_{EA} is the electron affinity; $23.06n$ converts the kilocalorie units to volt equivalents, n being the number of electrons transferred and -4.44 the ΔG° value for $H^+/\frac{1}{2}H_2$ (g).

Inorganic Chemistry

Second year
1st semester

Lecture 7

Dr. Ahlam Jameel Abdul-Ghani

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Electrochemistry
ELECTRODE POTENTIAL
PART 1

If we immerse a piece of zinc metal in pure water. A small number of zinc atoms go into solution as Zn(II) ions, leaving their electrons behind in the metal:

$Zn(s) \rightarrow Zn^{2+} + 2e^{-}$

As this process goes on, the electrons which remain in the zinc cause a negative charge to build up within the metal which makes it increasingly difficult for additional positive ions to leave the metallic phase. A similar buildup of positive charge in the liquid phase adds to this inhibition resulting in a solution in which the concentration of Zn^{2+} is still too low (around 10^{-10} *M*) to be detected by ordinary chemical methods

If we immerse the zinc in a solution of copper sulfate instead of pure water, the zinc metal quickly becomes covered with a black coating of finely-divided metallic copper. The reaction is a simple oxidation-reduction process, a transfer of two electrons from the zinc to the copper:

$$\mathrm{Zn}(s) \rightarrow \mathrm{Zn}^{2+} + 2e^{-} \qquad \mathrm{Cu}^{2+} + 2e^{-} \rightarrow \mathrm{Cu}(s)$$

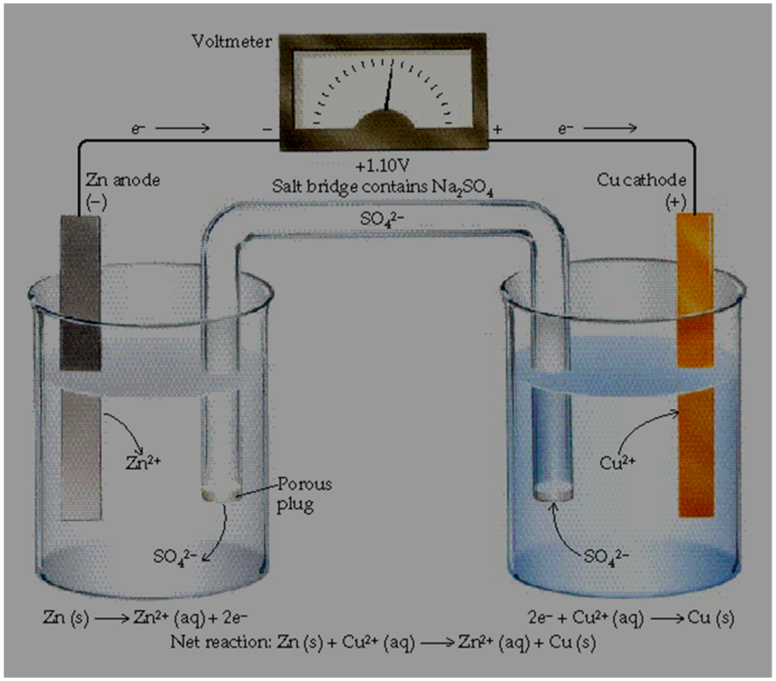
The dissolution of the zinc is no longer inhibited by a buildup of negative charge in the metal, because the excess electrons are removed from the zinc by copper ions that come into contact with it.

$$\mathrm{Zn}(s) + \mathrm{Cu}^{2+} \rightarrow \mathrm{Zn}^{2+} + \mathrm{Cu}(s)$$

Half Cell reaction: Chemical changes that involves only oxidation or reduction and the half cell contains only the oxidized and reduced forms of an element in contact with each other . A half cell contains a piece of metal(electrode) in a solution of its ion. The reduced and oxidized forms of the element are called the redox couple

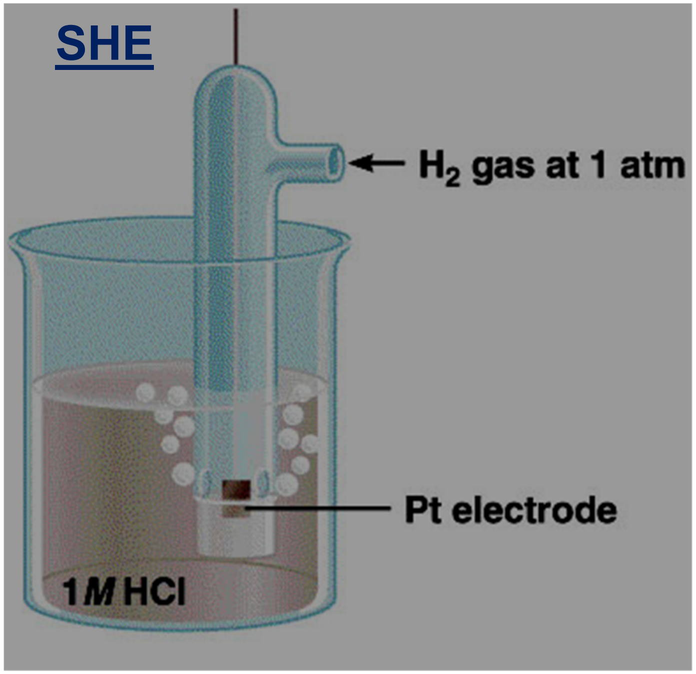
Connecting the electrodes of the two half cells by a conductive wire with an inserted voltmeter the potential difference will be measured by **measuring the sum of the two *half-cell potentials*.**

Electrochemical cell: A cell in which spontaneous oxidn-redn reactions produce electrical energy. They are **galvanic** or **voltaic cells**. an example is the **Daniel cell** or Zn-Cu cell Contact between the two compartments is made with a "**salt bridge**" : a glass tube filled with a firm jelly containing a suitable electrolyte such as K_2SO_4 ,or KNO_3 . The ions in the gelatin are still able to move. The copper and zinc plates (the **electrodes**) are linked by a conducting wire, which completes the circuit.



The difference in electrical potential between the anode and cathode is called: *cell voltage, electromotive force (emf), or cell potential (volts V)*

Since every oxidation must be followed by reduction , **it is impossible to measure the potential of a single electrode without using a reference electrode to measure the strength of the oxidizing or reducing agent**. We do it by arbitrarily setting *one redox half-reaction* to zero, and measuring all other cells with respect to this **arbitrary zero reference point. The universal reference standard for** electrochemistry is the **standard hydrogen electrode, or SHE**



This electrode contains a piece of metal electrically coated with a grainy black surface of inert Pt metal immersed in 1M H^+aq solution. H_2 gas is bubbled at 1 atm through a glass envelope over the platinized electrode

Reduction Reaction

$$2e^- + 2H^+aq\ (1\ M) \longrightarrow H_2\ (1\ atm)$$

$$E^0 = 0.0\ \text{V}$$

Standard Electrode Potentials

- **Cell potential(ΔE) (V) (voltage of the cell, emf):** A measure of the ability of a cell to force electrons through a circuit ***or the difference*** in electrical potential between the anode and cathode

Standard electrochemical cell (E^o_{cell}) :

A cell in which all reactants and products are in their thermodynamic **standard states 1** ***M for dissolved species*** (reactants and products) **and all gases are at partial pressure of 1 atm at 25^oC.**

Representation of cell:

$\mathrm{Zn}\ (s)\ |\ \mathrm{Zn}^{2+}\ (1\ M)\ \ ||\ \ \mathrm{Cu}^{2+}\ (1\ M)\ |\ \mathrm{Cu}\ (s)$

anode **Salt bridge** **cathode**

$2e^- + 2H^+aq\ (1\ M) \longrightarrow H_2\ (1 atm)$ **E ° =0.0 V** **reduction(*SHE* cathode)**

$H_2\ (1 atm) \longrightarrow 2e^- + 2H^+\ (1\ M)$ **E ° =0.0 V** **oxidation(*SHE* anode)**

By convention the potential associated with each electrode is the potential for reduction to occur at that electrode.
Thus standard electrode potentials are the standard reduction potentials denoted $E^{o}red$
The cell potential is given by (the standard reduction potential of the cathode reaction) - (the standard reduction potential of the anode reaction)

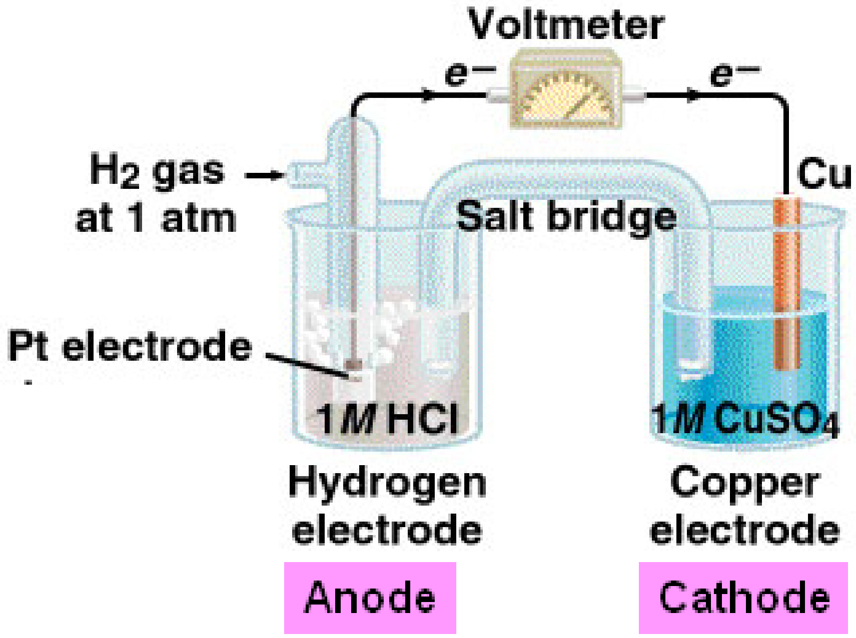
$$E^{o}cell = E^{o}red(cathode) - E^{o}red\ (anode)$$

Under standard conditions the emf is called the standard emf or the standard cell potential $E^{o}cell$. So for the Zn/Cu voltaic cell

$$Zn(s) + Cu^{2+}(aq,1M) \rightarrow Zn^{2+}(aq) + Cu(s)$$

$$E^{o}cell = +0.34 - (-0.76) = +1.10V$$

Standard Electrode Potentials



$$E^0_{cell} = E^0_{cathode} - E^0_{anode}$$

$$E^0_{cell} = E^0_{Cu^{2+}/Cu} - E^0_{H2/2H^+}$$

$$0.34 = E^0_{Cu^{2+}/Cu} - (0)$$

$$E^0_{Cu^{2+}/Cu} = 0.34 \text{ V}$$

$\mathrm{Pt}\ (s) \mid H_2\ (1\ atm) \mid H^+\ (1\ M) \parallel Cu^{2+}\ (1\ M) \mid \mathrm{Cu}\ (s)$

Anode (oxidation): $H_2\ (1\ atm) \longrightarrow 2H^+\ (1\ M) + 2e^-$

Cathode (reduction): $2e^- + Cu^{2+}\ (1\ M) \longrightarrow \mathrm{Cu}\ (s)$

$H2\ (1\ atm) + Cu^{2+}\ (1\ M) \longrightarrow \mathrm{Cu}\ (s) + 2H^+\ (1\ M)$

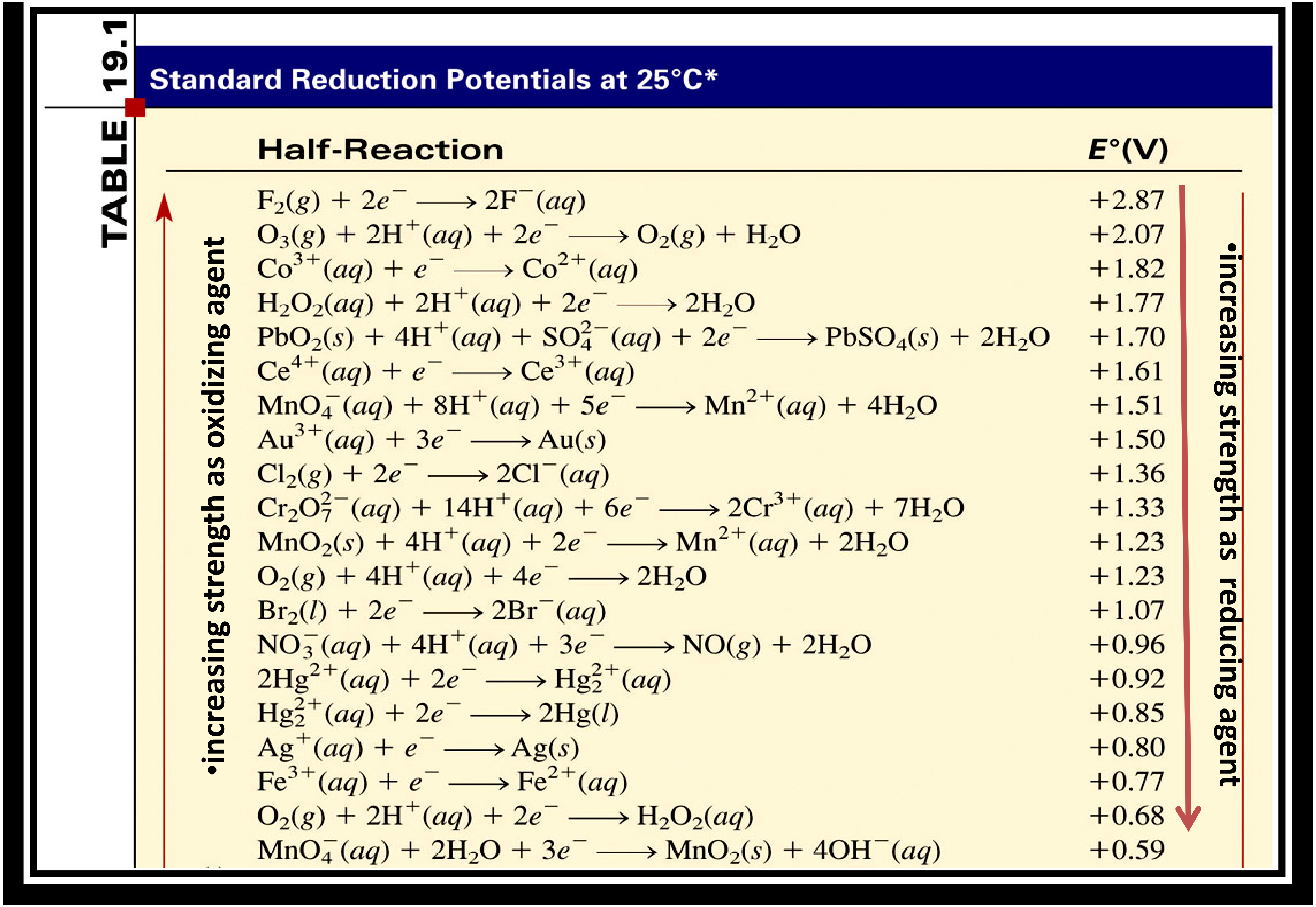


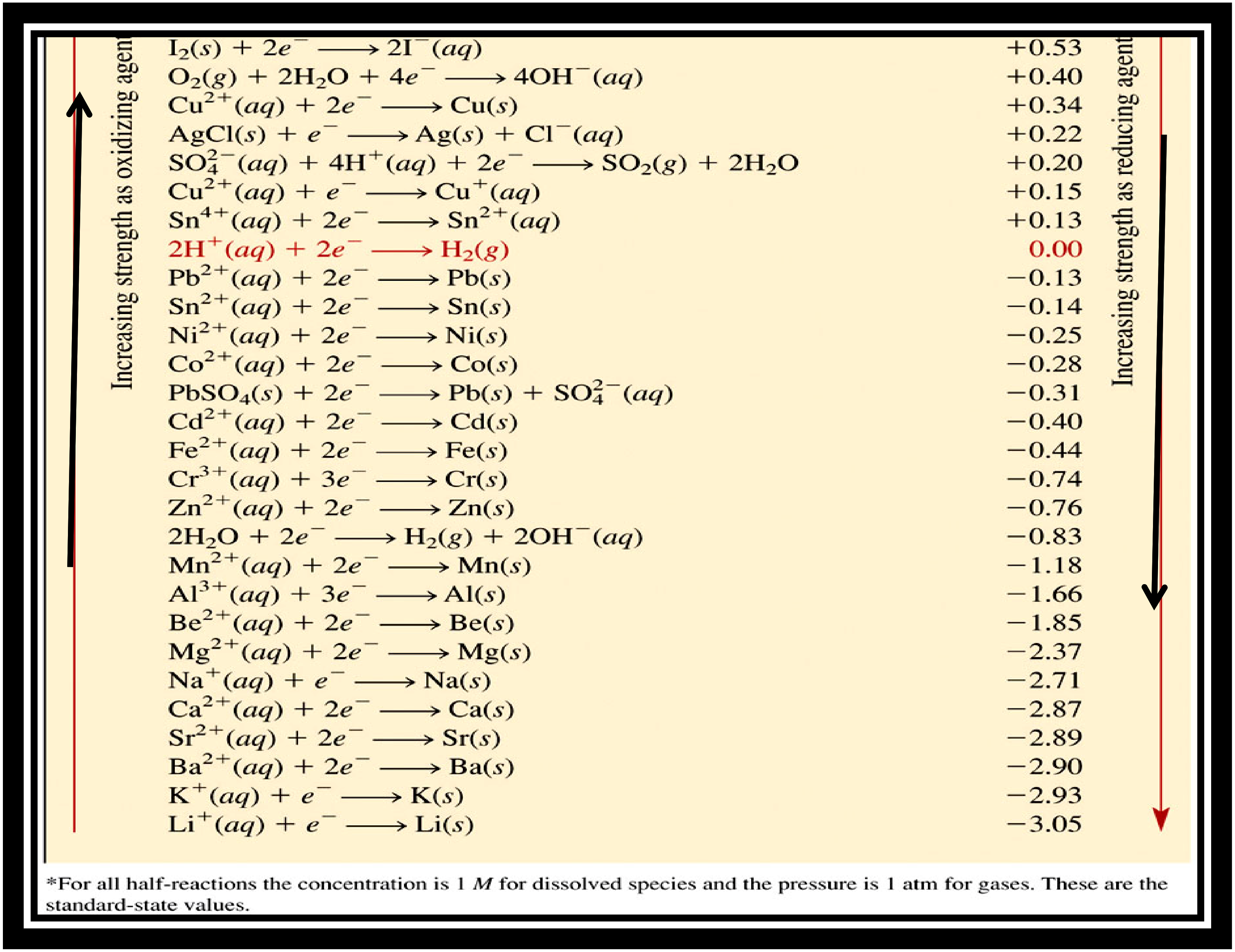
TABLE 19.1

Standard Reduction Potentials at 25°C*

•increasing strength as oxidizing agent

Half-Reaction	$E°$(V)
$F_2(g) + 2e^- \longrightarrow 2F^-(aq)$	+2.87
$O_3(g) + 2H^+(aq) + 2e^- \longrightarrow O_2(g) + H_2O$	+2.07
$Co^{3+}(aq) + e^- \longrightarrow Co^{2+}(aq)$	+1.82
$H_2O_2(aq) + 2H^+(aq) + 2e^- \longrightarrow 2H_2O$	+1.77
$PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O$	+1.70
$Ce^{4+}(aq) + e^- \longrightarrow Ce^{3+}(aq)$	+1.61
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O$	+1.51
$Au^{3+}(aq) + 3e^- \longrightarrow Au(s)$	+1.50
$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$	+1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O$	+1.33
$MnO_2(s) + 4H^+(aq) + 2e^- \longrightarrow Mn^{2+}(aq) + 2H_2O$	+1.23
$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O$	+1.23
$Br_2(l) + 2e^- \longrightarrow 2Br^-(aq)$	+1.07
$NO_3^-(aq) + 4H^+(aq) + 3e^- \longrightarrow NO(g) + 2H_2O$	+0.96
$2Hg^{2+}(aq) + 2e^- \longrightarrow Hg_2^{2+}(aq)$	+0.92
$Hg_2^{2+}(aq) + 2e^- \longrightarrow 2Hg(l)$	+0.85
$Ag^+(aq) + e^- \longrightarrow Ag(s)$	+0.80
$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	+0.77
$O_2(g) + 2H^+(aq) + 2e^- \longrightarrow H_2O_2(aq)$	+0.68
$MnO_4^-(aq) + 2H_2O + 3e^- \longrightarrow MnO_2(s) + 4OH^-(aq)$	+0.59

•increasing strength as reducing agent



Increasing strength as oxidizing agent

$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$	+0.53
$O_2(g) + 2H_2O + 4e^- \longrightarrow 4OH^-(aq)$	+0.40
$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$	+0.34
$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-(aq)$	+0.22
$SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \longrightarrow SO_2(g) + 2H_2O$	+0.20
$Cu^{2+}(aq) + e^- \longrightarrow Cu^+(aq)$	+0.15
$Sn^{4+}(aq) + 2e^- \longrightarrow Sn^{2+}(aq)$	+0.13
$2H^+(aq) + 2e^- \longrightarrow H_2(g)$	0.00
$Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s)$	−0.13
$Sn^{2+}(aq) + 2e^- \longrightarrow Sn(s)$	−0.14
$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$	−0.25
$Co^{2+}(aq) + 2e^- \longrightarrow Co(s)$	−0.28
$PbSO_4(s) + 2e^- \longrightarrow Pb(s) + SO_4^{2-}(aq)$	−0.31
$Cd^{2+}(aq) + 2e^- \longrightarrow Cd(s)$	−0.40
$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$	−0.44
$Cr^{3+}(aq) + 3e^- \longrightarrow Cr(s)$	−0.74
$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$	−0.76
$2H_2O + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$	−0.83
$Mn^{2+}(aq) + 2e^- \longrightarrow Mn(s)$	−1.18
$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$	−1.66
$Be^{2+}(aq) + 2e^- \longrightarrow Be(s)$	−1.85
$Mg^{2+}(aq) + 2e^- \longrightarrow Mg(s)$	−2.37
$Na^+(aq) + e^- \longrightarrow Na(s)$	−2.71
$Ca^{2+}(aq) + 2e^- \longrightarrow Ca(s)$	−2.87
$Sr^{2+}(aq) + 2e^- \longrightarrow Sr(s)$	−2.89
$Ba^{2+}(aq) + 2e^- \longrightarrow Ba(s)$	−2.90
$K^+(aq) + e^- \longrightarrow K(s)$	−2.93
$Li^+(aq) + e^- \longrightarrow Li(s)$	−3.05

Increasing strength as reducing agent

*For all half-reactions the concentration is 1 *M* for dissolved species and the pressure is 1 atm for gases. These are the standard-state values.

Balance the following reaction between MnO_4^-(permanganate) and $C_2O_4^{2-}$ (oxalate) in acidic solution:

$MnO_4^-(aq) + C_2O_4^{2-}(aq) \longrightarrow Mn^{2+}(aq) + CO_2(aq)$

for the half reaction

$MnO_4^- \longrightarrow Mn^{2+}$ reduction half reaction

$MnO_4^- \longrightarrow 4H_2O + Mn^{2+}$

$C_2O_4^{2-}(aq) \longrightarrow 2CO_2(aq) + 2e$ …………..(1) oxidation half reaction

To balance the hydrogen, add 8 H^+ to the left side.

$8H^+ + MnO_4^- \longrightarrow Mn^{2+} + 4H_2O$

to balance charge we add 5e to the left side

$5e + 8H^+ + MnO_4^- \longrightarrow Mn^{2+} + 4H_2O$ …………(2) x2

reduction half reaction

$C_2O_4^{2-}(aq) \longrightarrow 2CO_2(aq) + 2e$ …………………..(1) x5

oxidation half reaction

Combining the Half-Reactions:

$10e + 16\,H^+ + 2\,MnO_4^- \;\; + 5\,C_2O_4^{2-}\,(aq) \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O + 10e$

the balanced reaction is:

$16\,H^+ + 2\,MnO_4^- \;\; + 5\,C_2O_4^{2-}(aq) \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$

Problem example

Work out and balance the following reactions in standard acid solution

$MnO_4^-(aq) + HSO_3^-(aq) \rightarrow Mn^{2+}(aq) + SO_4^{2-}(aq)$

$[MnO_4^- + 8H^+ + 5e \rightarrow Mn^{2+}(aq) + 4H_2O] \quad \times 2$

$[HSO_3^- + H_2O \rightarrow SO_4^{=} + 2e + 3H^+] \quad \times 5$

$2MnO_4^-(aq) + 5HSO_3^-(aq) + \;\; H^+ \;\; \rightarrow 2Mn^{2+}(aq) + 5\,SO_4^{2-}(aq) \;\; + 3\,H_2O$

Cell potentials and free energy (thermodynamics)

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

ΔH= Change in enthalpy

ΔS= Change in entropy

Because emf, (E) of a redox reaction is an indication of the spontaneity of the reaction there is a relationship between ΔG and E

ΔG for a redox reaction can be found by using the equation

$\Delta G = - nFE$

where n is the number of moles of electrons transferred, and F is a constant, the Faraday.

1 F = 96485 C/mol = 96485 J/V. mol= 23.06 Kcal/V.mol= N(av) x e

Under standard conditions

$\Delta G^\circ = - nFE^\circ$

which relates the standard emf E^o to the standard fre energy change ΔG°

ΔG° is also related to the equilibrium constant K

$\Delta G^\circ = - RT \text{ In } K$

Nernst Equation

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

This means

$-n FE = -nFE^\circ + RT \ln Q$

Dividing both sides by -nF, we get the Nernst equation

$$\mathbf{E = E° - \frac{\mathit{RT}}{\mathit{nF}} \ln Q}$$

Nernst equation

E° = standard electrode potential, R = gas constant (8.31 J/mol.K), T = temperature (Kelvins), n = moles of electr

F = Faraday constant (96485 Coul/mol)

$$E = E^0 - \frac{RT}{nF}\ln\frac{[\mathrm{products}]}{[\mathrm{reactants}]}$$

$$E = E^0 - \frac{RT}{nF}\ln\frac{[\text{products}]}{[\text{reactants}]}$$

$$E = E^\circ - \frac{2.303RT}{nF}\log_{10}\frac{[products]}{[reactants]}$$

$$\frac{2.303RT}{F} = 0.0592\ \text{V. mol}$$

$$E = E^\circ - \frac{0.0592}{n}\log_{10}\frac{[C]^c[D]^d}{[A]^a[B]^b}$$

For the reaction
aA + bB ⇆ cC + dD

Standard Electrode Potentials & Equilibrium Constants

- **Galvanic cells produce current because the net cell reaction is *not* at equilibrium**

$$E = E^0 - 0.0592 / n \bullet \log Q$$ **anytime**

$$E_{cell} = 0 = E^0 - 0.0592 / n \bullet \log K$$ **at equilibrium**

$$E^0 = 0.0592 / n \bullet \log K$$

Spontaneity of Redox Reactions

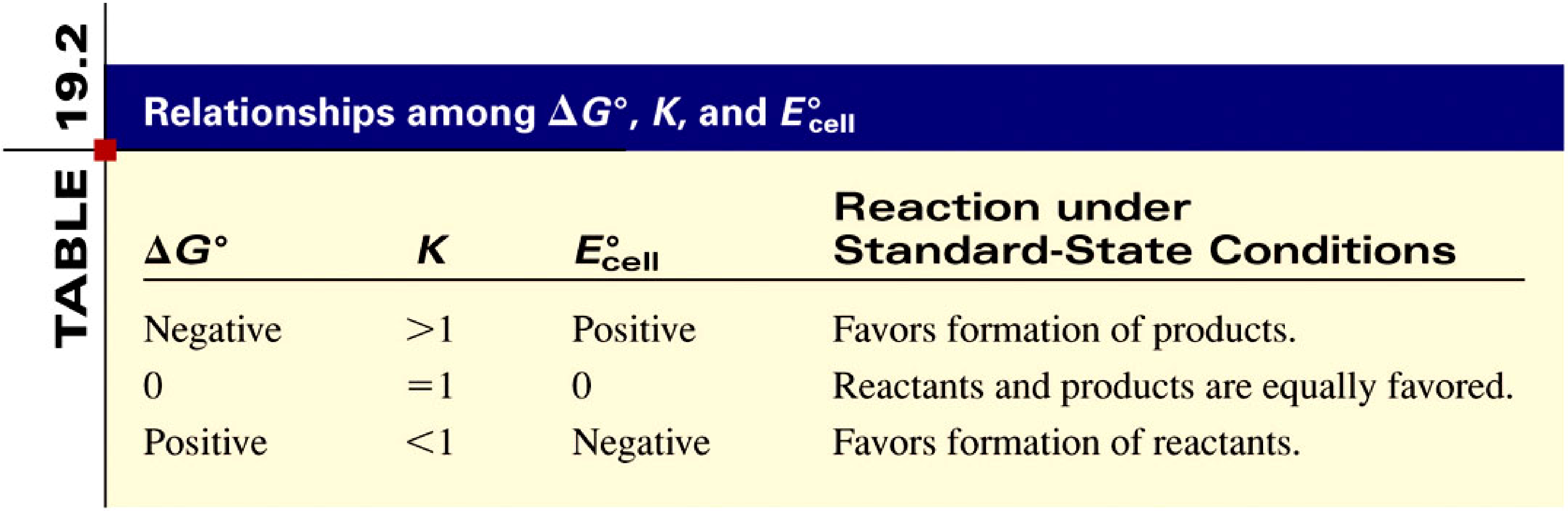


TABLE 19.2

Relationships among $\Delta G°$, K, and $E°_{cell}$

$\Delta G°$	K	$E°_{cell}$	Reaction under Standard-State Conditions
Negative	>1	Positive	Favors formation of products.
0	$=1$	0	Reactants and products are equally favored.
Positive	<1	Negative	Favors formation of reactants.

Inorganic Chemistry

Second year
1st semester

LECTURE 9

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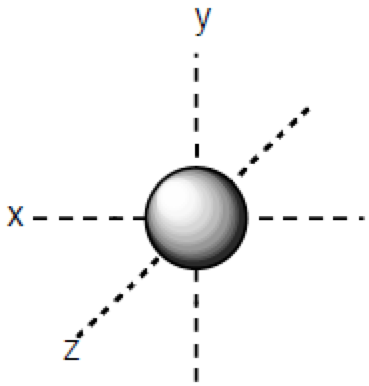
Symmetry

Symmetry is when one shape becomes exactly like another if you flip, slide or turn it.

The quality of something that has two sides or halves that are the same or very close in size, shape, and position : the quality of having symmetrical parts

Having a structure that exhibits a regular repeated pattern of the component parts



Symmetry can be described in terms of two distinct parts

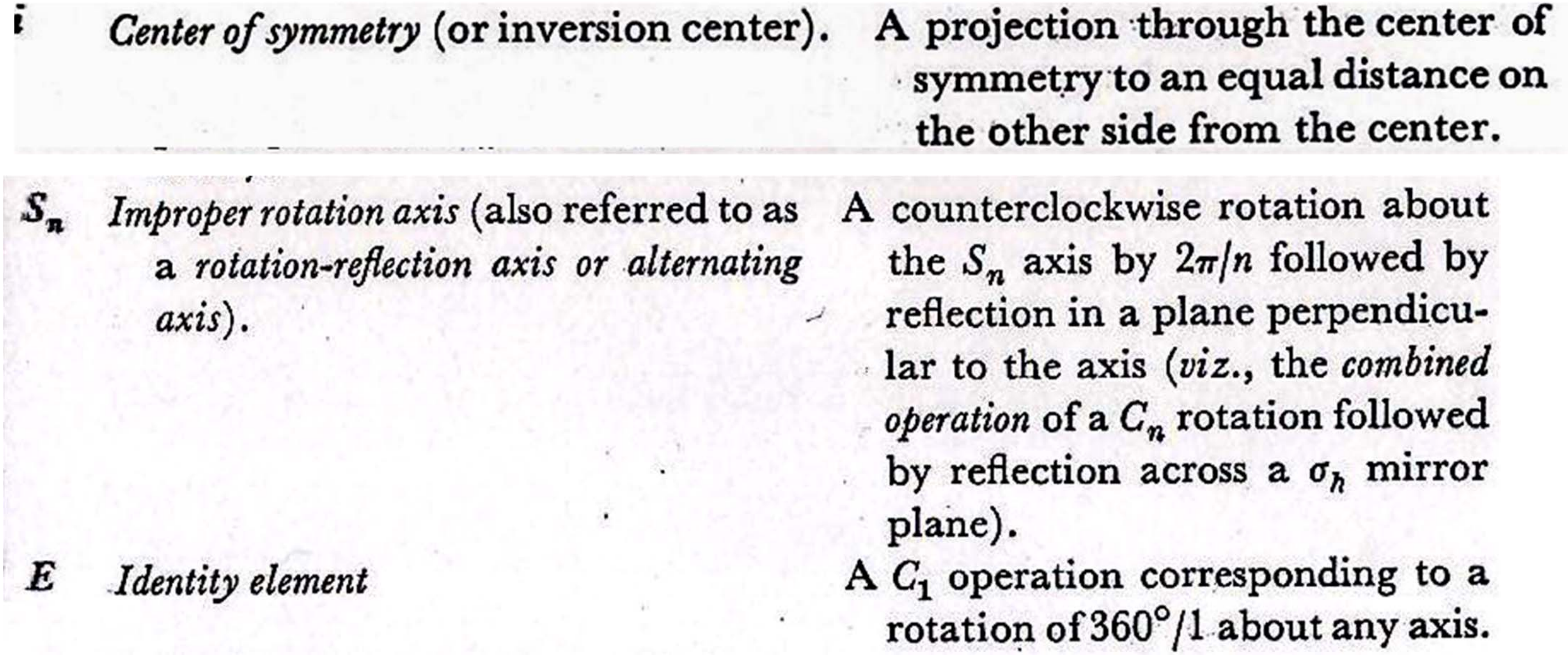
1-Symmetry Operations 2- Symmetry Elements

1-A symmetry operation is a movement of an object/molecule that leaves it in an equivalent configuration.

2-A symmetry element is an imaginary line, point or plane about which a symmetry operation is performed. Note that all elements pass through the center of the object

Symmetry Elements and Associated Operations

Symbol	Element	Operation
C_n	*Proper rotation axis*	A counterclockwise rotation about the C_n axis by $2\pi/n$ (or $360°/n$).
σ_h	*Horizontal mirror plane* perpendicular to principal C_n axis (*i.e.*, proper axis of highest symmetry).	Reflection across the plane of symmetry.
σ_v	*Vertical mirror plane* containing the principal C_n axis.	Reflection across the plane of symmetry.
σ_d	*Diagonal mirror*, containing the principal C_n axis; the plane bisects the angle formed by two horizontal C_2 axes which are perpendicular to the principal axis C_n of highest symmetry.	Reflection across the plane of symmetry.



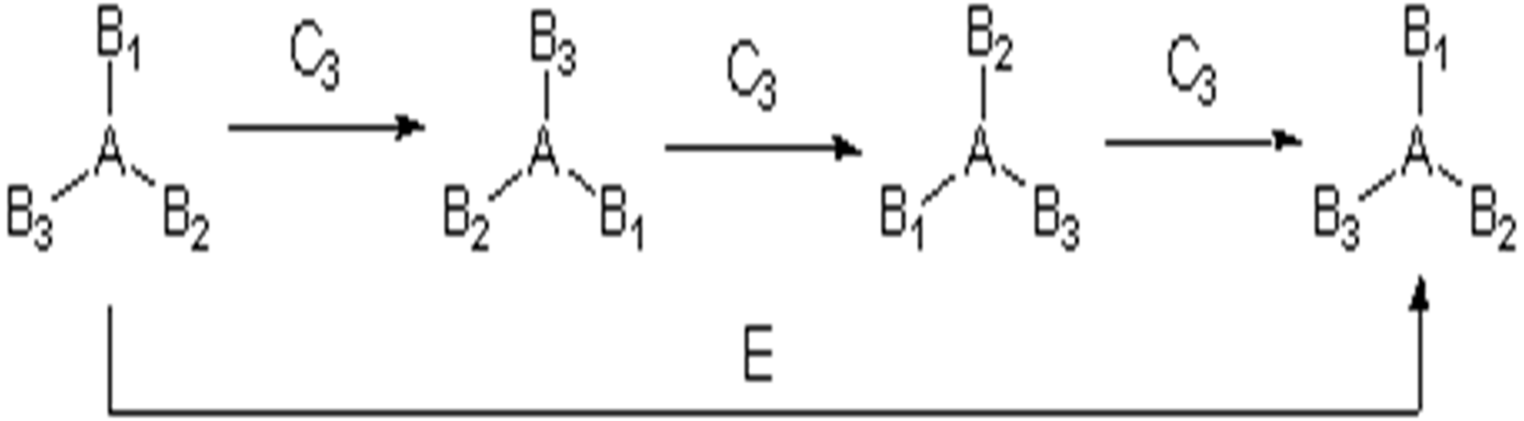
i	*Center of symmetry* (or inversion center).	A projection through the center of symmetry to an equal distance on the other side from the center.
S_n	*Improper rotation axis* (also referred to as a *rotation-reflection axis or alternating axis*).	A counterclockwise rotation about the S_n axis by $2\pi/n$ followed by reflection in a plane perpendicular to the axis (*viz.*, the *combined operation* of a C_n rotation followed by reflection across a σ_h mirror plane).
E	*Identity element*	A C_1 operation corresponding to a rotation of 360°/1 about any axis.

Identity Operation : E

The identity operation leaves the molecule or object unchanged. The operation is performed about the object itself and exists for every object.

The identity is also generated by carrying out any other operations in succession

For example, these operations result in E: C_n^n, S_n^n (n even), Sn^{2n} (n odd), s^2, i^2



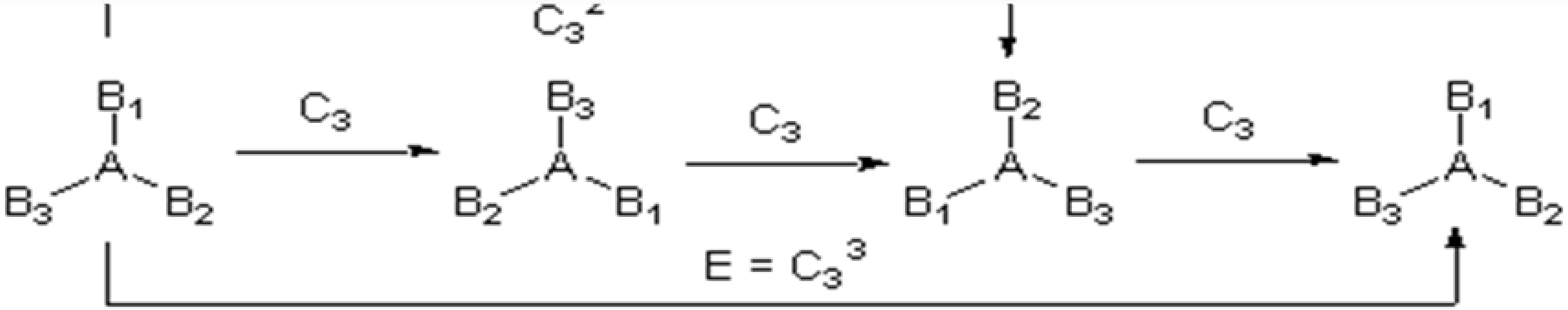
performing a C_3 rotation 3 times (C_3^3) results in the identity operation E

Rotation about an *n*-fold axis of symmetry

The symmetry operation of rotation about an n-fold axis (the symmetry element) is denoted by the symbol C_n, in which the angle of rotation is $\frac{360^\circ}{n}$; n is an integer, e.g. 2, 3 or 4. Applying this notation to the BF_3 molecule in Figure 3.1 gives a value of $n = 3$ (equation 3.1), and therefore we say that the BF_3 molecule contains a C_3 *rotation axis*; in this case, the axis lies perpendicular to the plane containing the molecule.

$$\text{Angle of rotation} = 120^\circ = \frac{360^\circ}{n} \qquad (3.1)$$

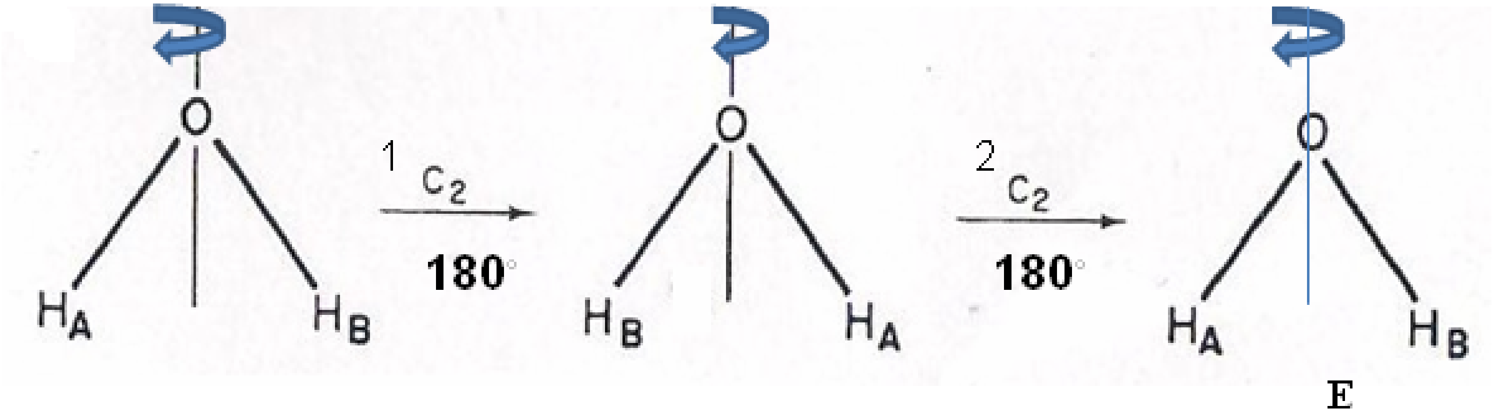
Fig. 3.1 Rotation of the trigonal planar BF$_3$ molecule through 120° generates a representation of the structure that is indistinguishable from the first; one F atom is marked in red simply as a label. A second 120° rotation gives another indistinguishable structural representation.



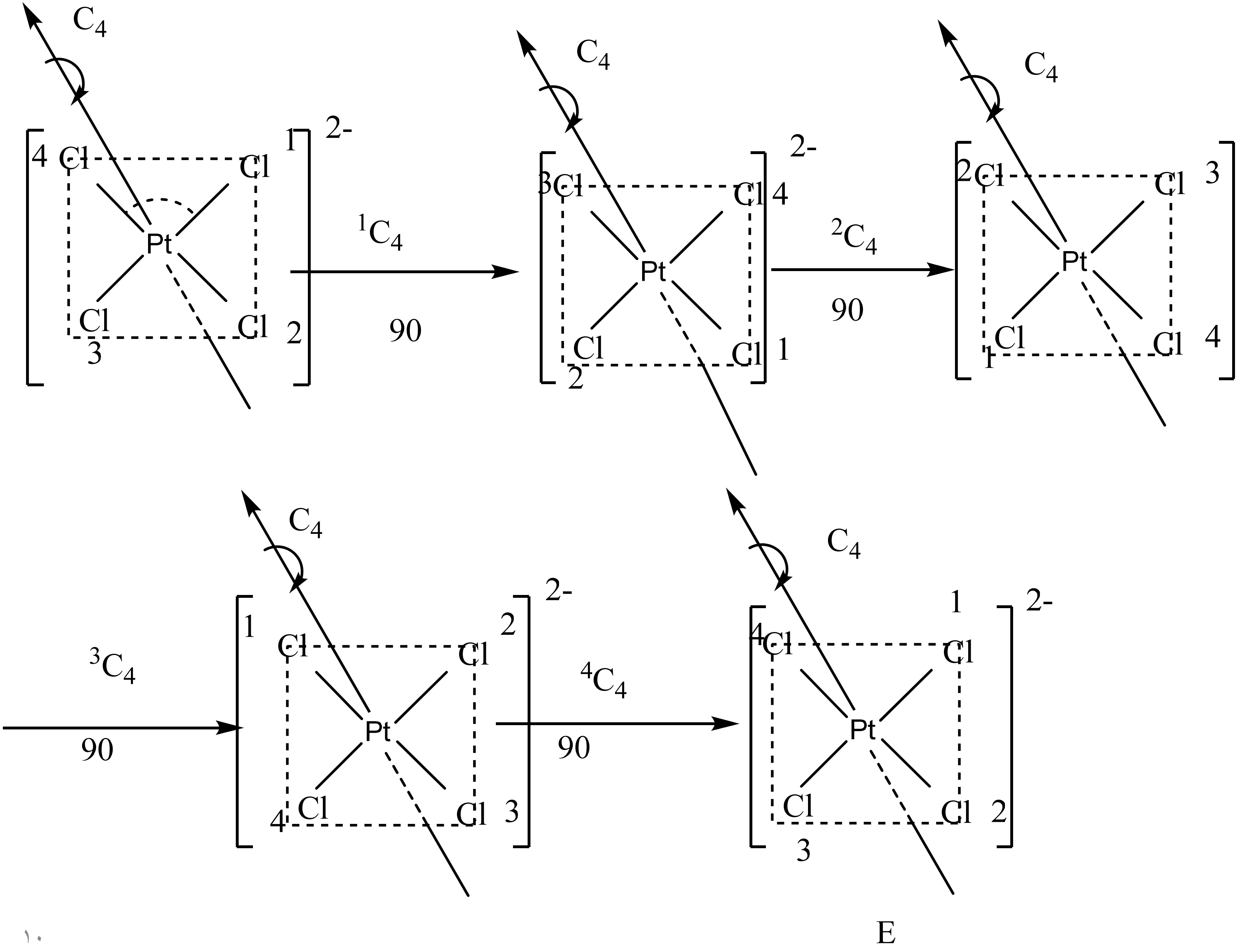
Rotation about a C_3 axis

If a molecule possesses more than one type of *n*-axis, the axis of highest value of *n* is called the *principal axis*; it is the axis of *highest molecular symmetry*.

Angular molecules: H_2O, SO_2, NO_2, NO_2^-, H_2S, $R_2O(S)$

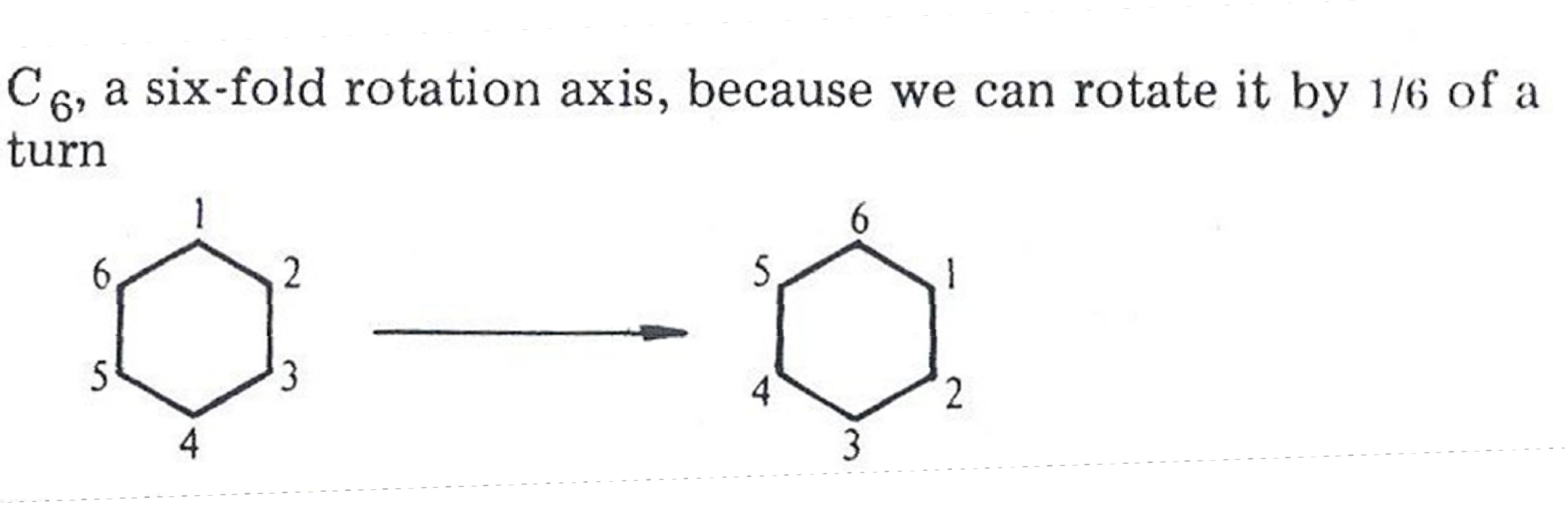


Two fold symmetry C_2 rotation (n= 360/180)



C4
2-
4
Cl
1
Pt
3
2
$^1C_4$
90
$^2C_4$
$^3C_4$
$^4C_4$
E

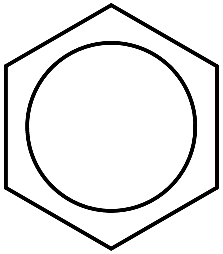
Hexagonal planes n= 360/60 = 6

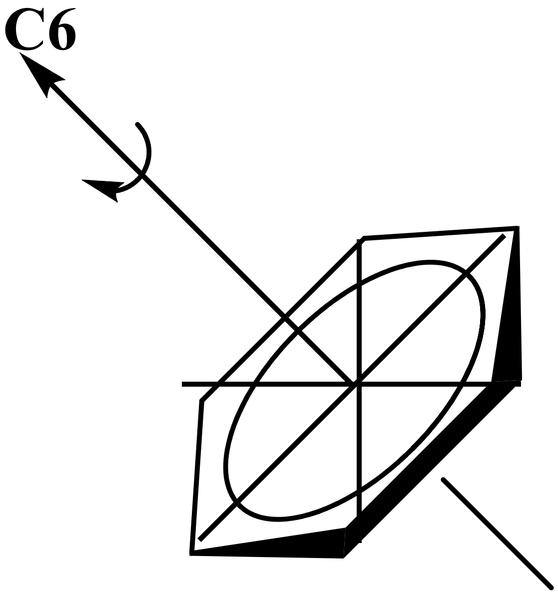


C_6, a six-fold rotation axis, because we can rotate it by 1/6 of a turn

Examples

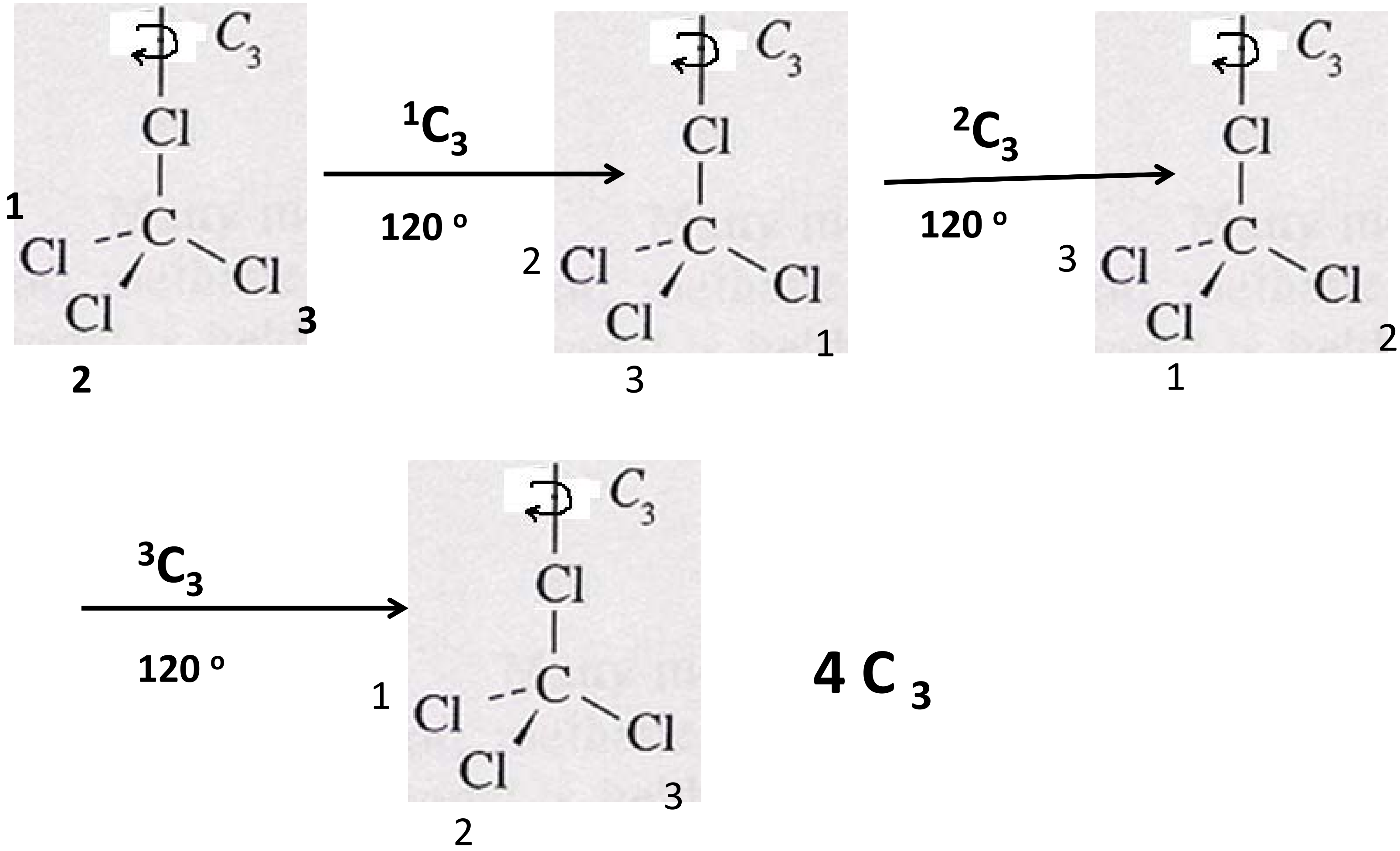
C_6H_6, C_6Cl_6





$C_6 \quad C_6^2 \quad C_6^3 \quad C_6^4 \quad C_6^5 \quad C_6^6$

Tetrahedral CH_4, CCl_4, $SiCl_4$, $SO_4^{=}$, ClO_4^{-}
(SP^3) (109.4 °)



$4\ C_3$

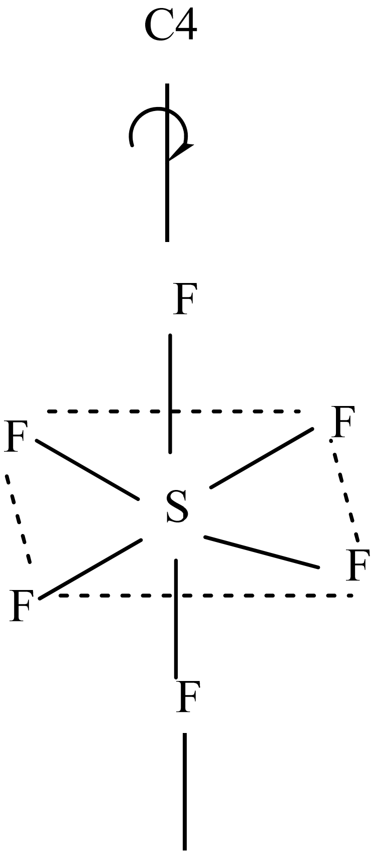
E

Octahedral

SF_6 , $[Co(H_2O)_6]^{2+}$, $[SiF_6]^{2-}$ (SP^3d^2) , $[Co(NH_3)_6]^{3+}$ (d^2sp^3)

n= 360/90= 4 C_4

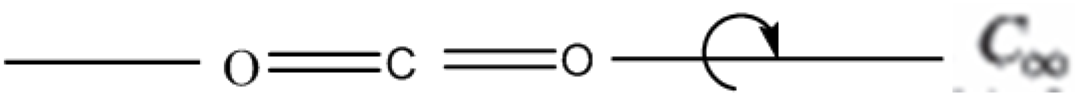
3 C_4 (X, Y, Z-axes)



Linear molecules

$H-C\equiv C-H$ $H-C\equiv N$ $H-Cl$

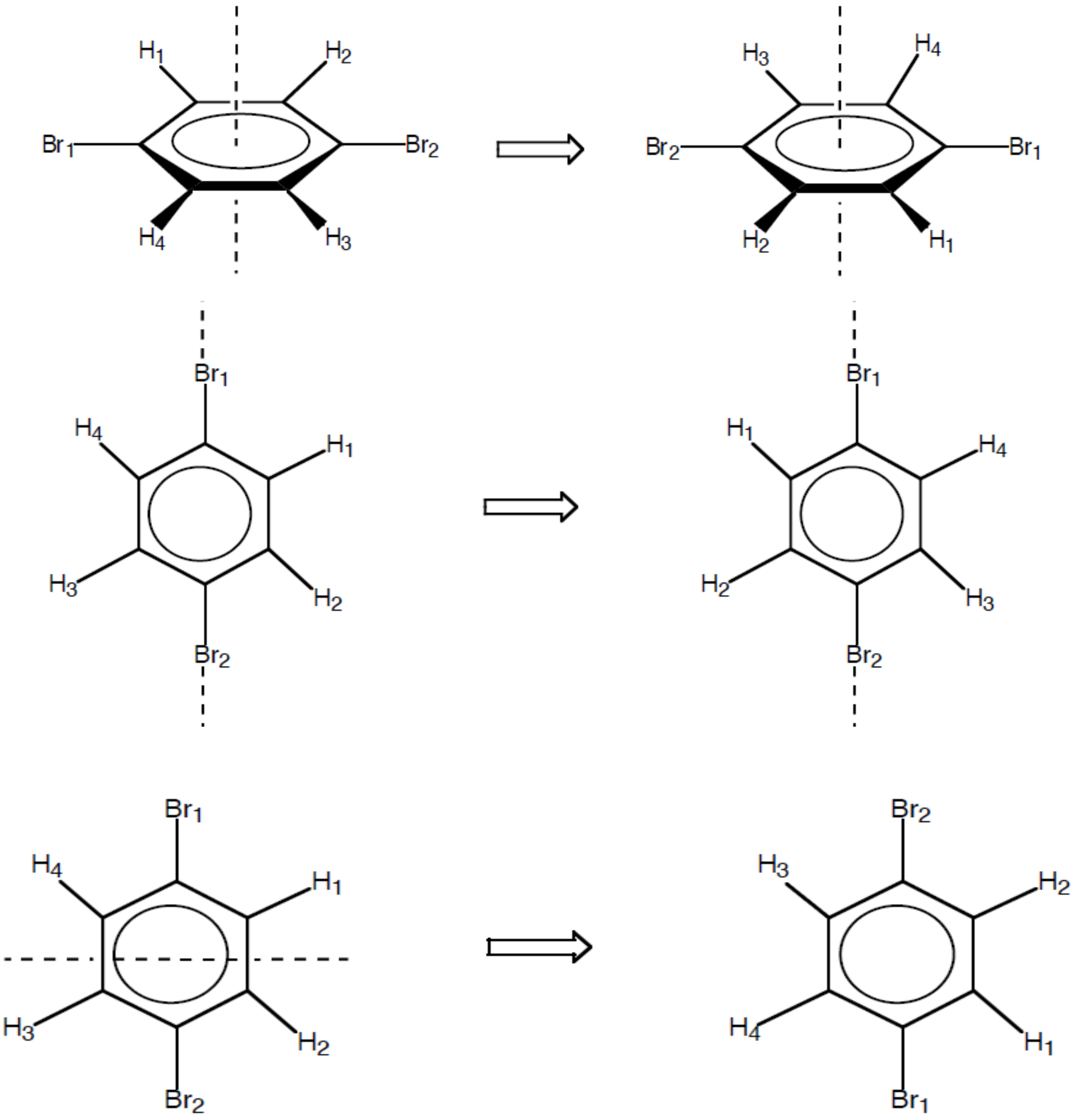
N_2 $O=O$ $H-H$

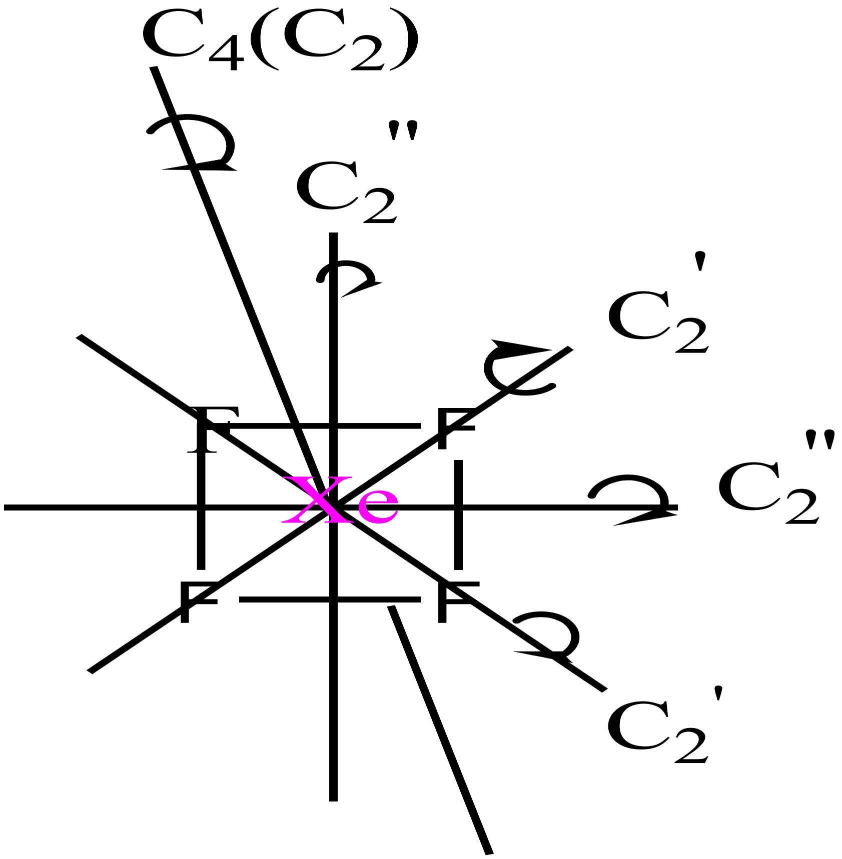


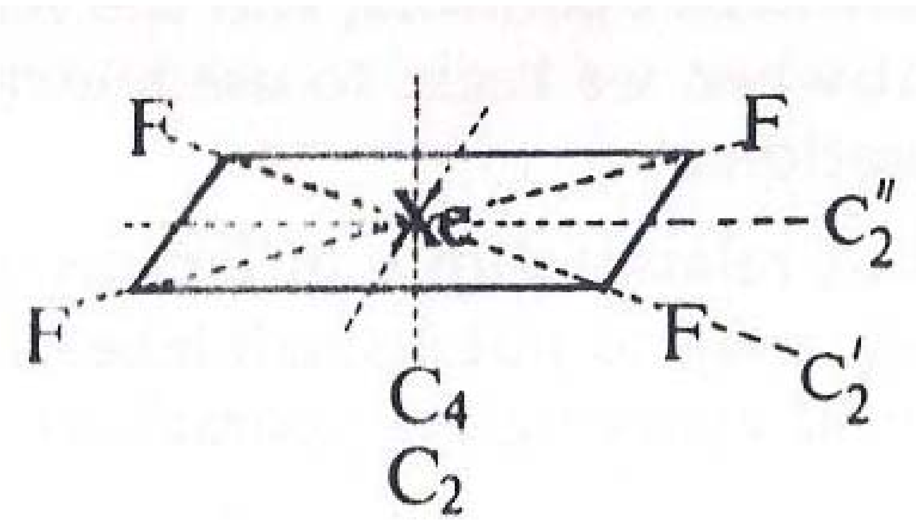
NO_2^+ (SP) , I_3^- , XeF_2, ICl_2^- (SP^3d) , N_2O (SP)

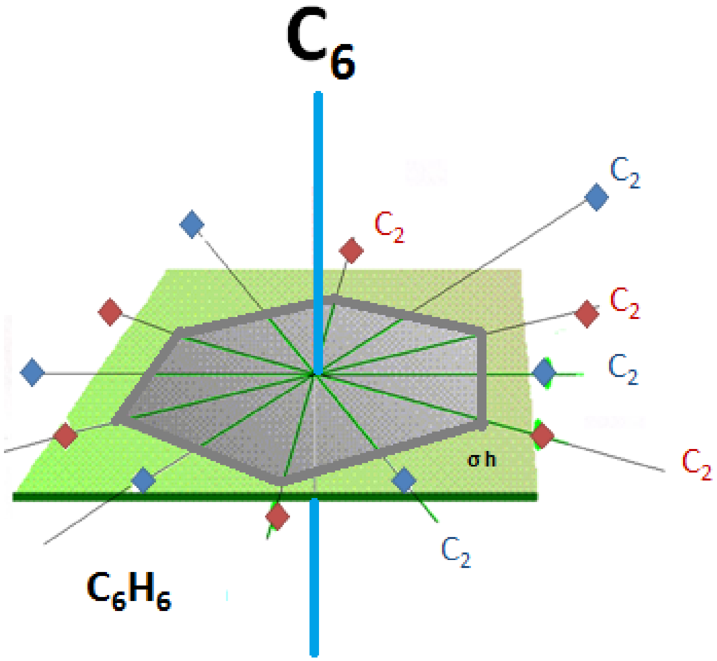
n= 360/0 Linear molecules the axis of the molecule passes through the molecule

C_2 Rotation Axes




C4(C2)
C2''
C2'
C2''
C2'
F
F
F
F
Xe


F
F
Xe
C2''
F
F
C2'
C4
C2

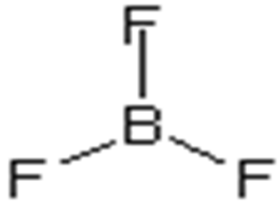

C6
C2
C2
C2
C2
C2
C2
C2
σ h
C6H6

Inversion center: or center of symmetry(i)

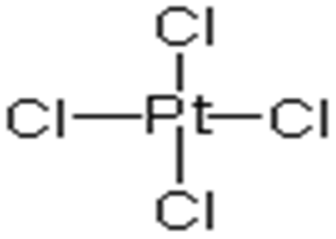
Reflection of points through the center of the object to positions equidistant on the opposite side

Only one inversion point can exist in an object

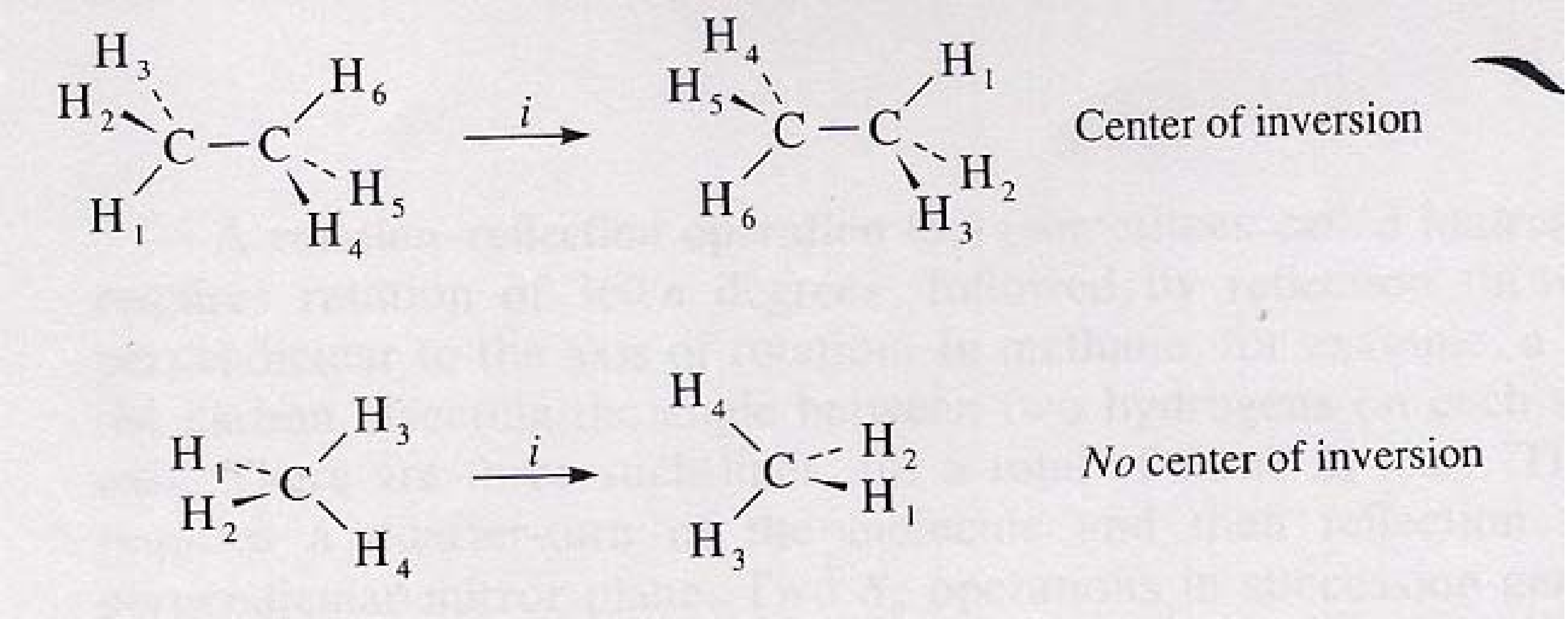
$i^2 = E$, i^n (n even) = E , i^n (n odd) = i



no inversion center



possesses an inversion center

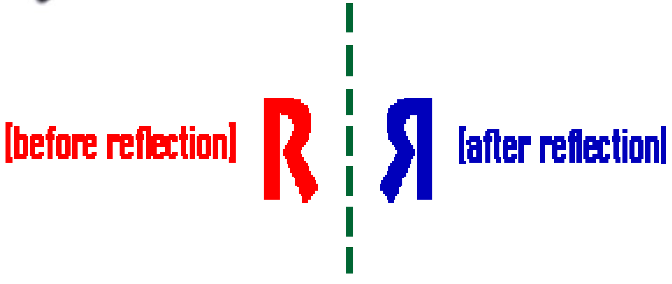


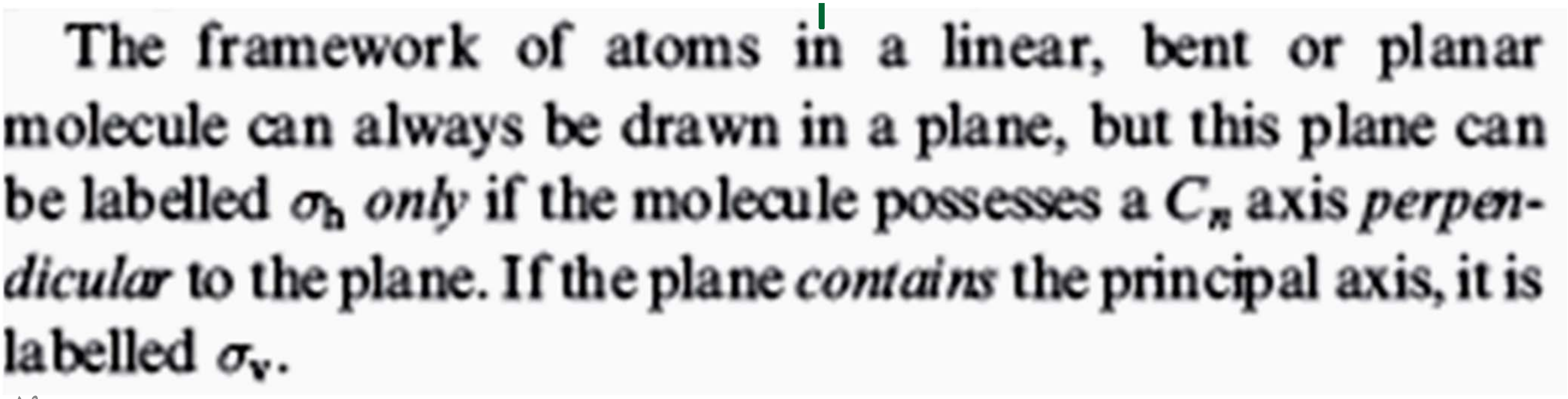
A center of symmetry: A point at the center of the molecule. It is not necessary to have an atom in the center (benzene, ethane) .

Tetrahedral, triangles, pentagons don't have a center of inversion symmetry

Reflection through a plane of symmetry (mirror plane)

If reflection of all parts of a molecule through a plane produces an indistinguishable configuration, the plane is a *plane of symmetry*; the symmetry operation is one of reflection and the symmetry element is the mirror plane (denoted by σ).





The framework of atoms in a linear, bent or planar molecule can always be drawn in a plane, but this plane can be labelled σ_h *only* if the molecule possesses a C_n axis *perpendicular* to the plane. If the plane *contains* the principal axis, it is labelled σ_v.

σ_h *Horizontal mirror plane* perpendicular to principal C_n axis (*i.e.*, proper axis of highest symmetry).

σ_v *Vertical mirror plane* containing the principal C_n axis.

σ_d *Diagonal mirror*, containing the principal C_n axis; the plane bisects the angle formed by two horizontal C_2 axes which are perpendicular to the principal axis C_n of highest symmetry.

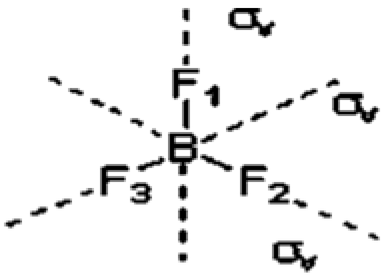
Reflection mirror or mirror plane: σ

Reflection of points through a plane to equidistant positions on the other side

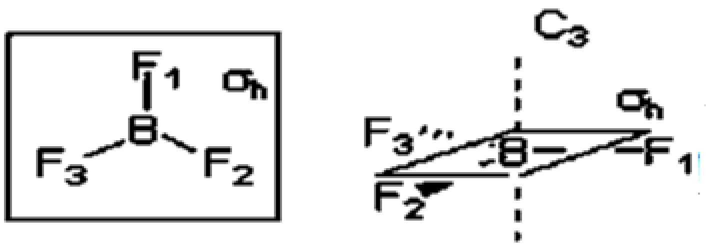
$\sigma^2 = E$, σ^n (n even) $= E$, σ^n (n odd) $= \sigma$

A mirror plane perpendicular on a principle rotation axis is labeled σ_h

A mirror plane that contains the principle rotation axis (C_n) is labeled σ_v or σ_d. There will always be n of these based on C_n



position of σ_v's in BF_3

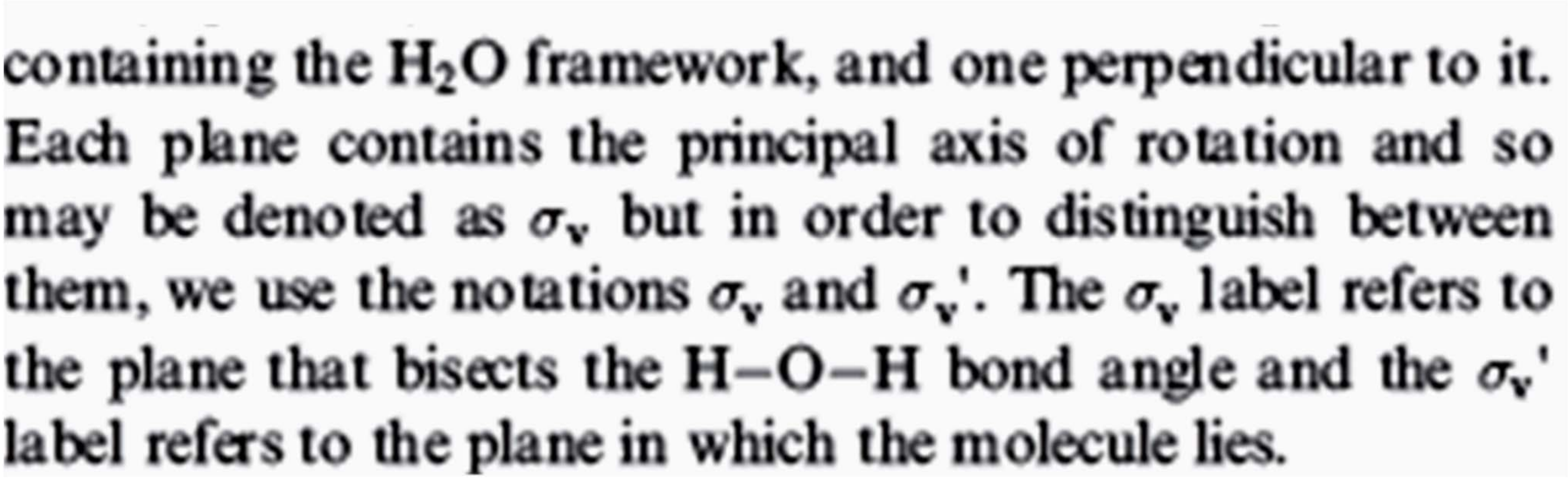


position of σ_h in BF_3

1-σ_v

a-H_2O molecule or any angular molecule

This possesses a C_2 axis but it also contains two mirror planes:



containing the H_2O framework, and one perpendicular to it. Each plane contains the principal axis of rotation and so may be denoted as σ_v but in order to distinguish between them, we use the notations σ_v and σ_v'. The σ_v label refers to the plane that bisects the H–O–H bond angle and the σ_v' label refers to the plane in which the molecule lies.

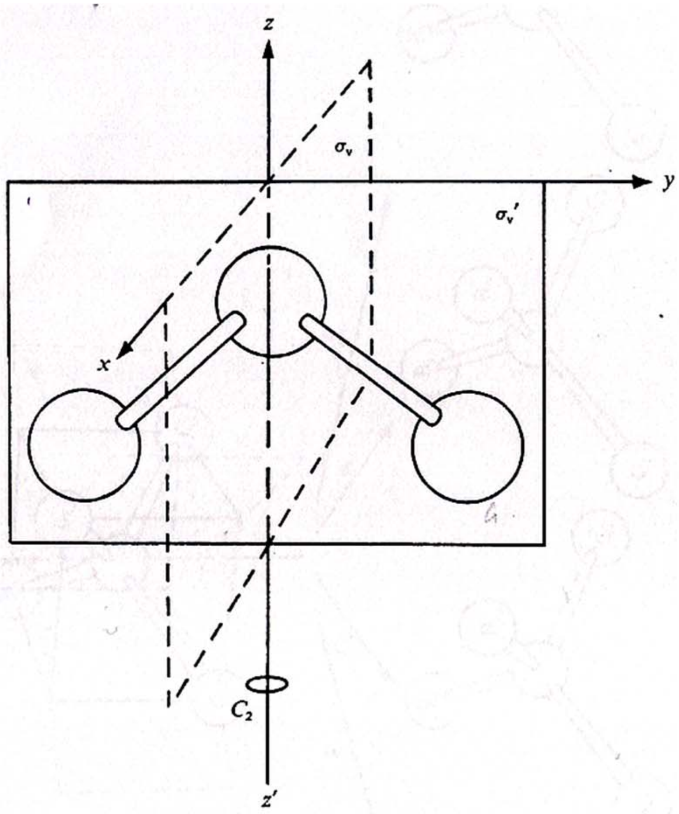
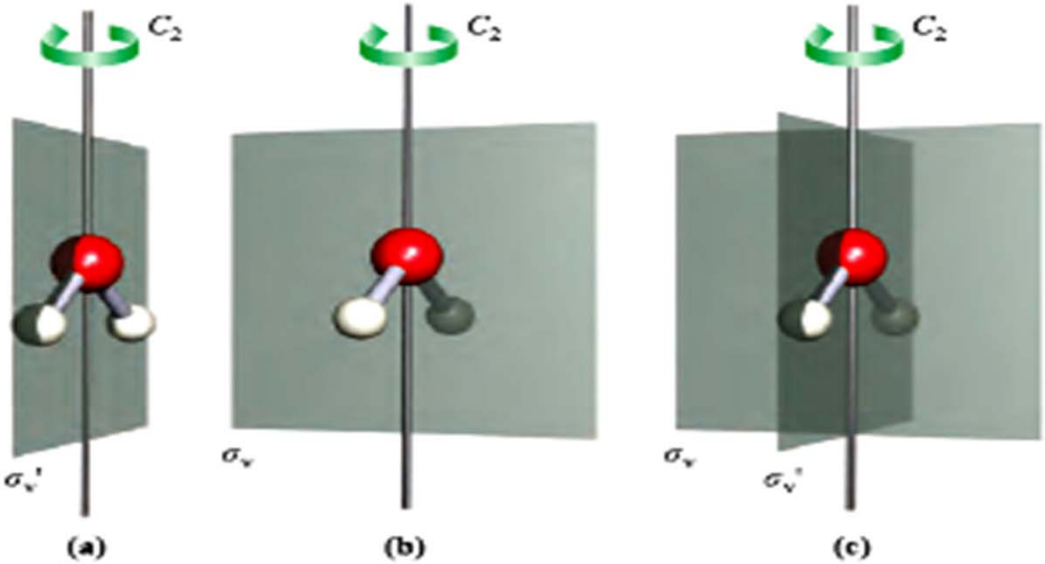
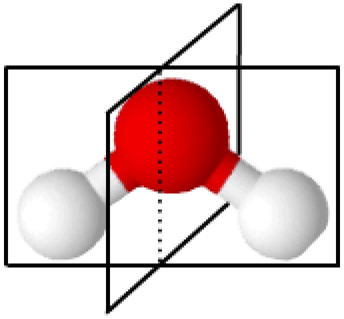


Fig. 3.1. Symmetry elements for H_2O (C_{2v})

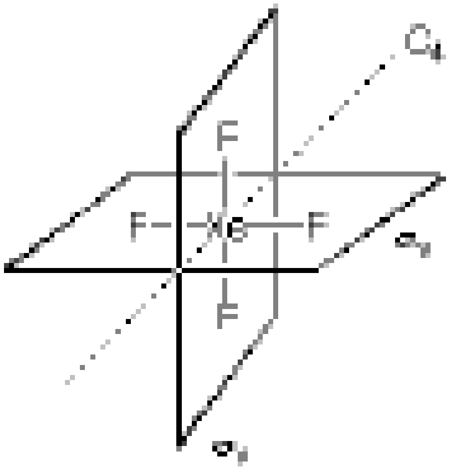


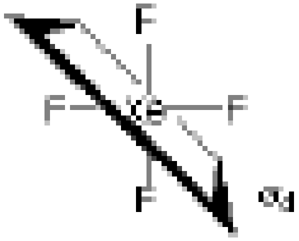
(a) (b) (c)

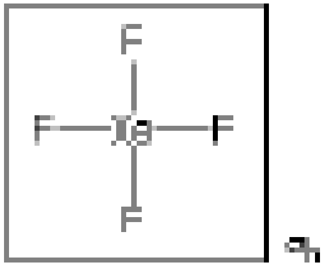
Fig. 3.3 The H_2O molecule possesses one C_2 axis and two mirror planes. (a) The C_2 axis and the plane of symmetry that contains the H_2O molecule. (b) The C_2 axis and the plane of symmetry that is perpendicular to the plane of the H_2O molecule. (c) Planes of symmetry in a molecule are often shown together on one diagram; this representation for H_2O combines diagrams (a) and (b).



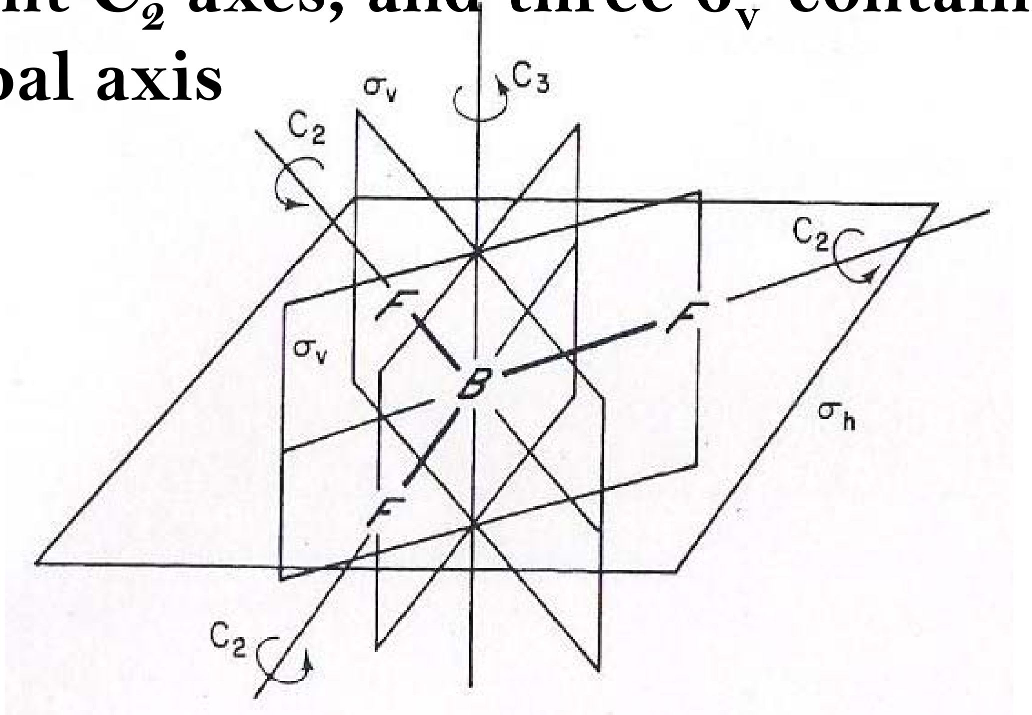
B-XeF_4 is square planar. It has four different C_2 axes. A C_4 axis out of the page is called the **principle axis** because it has the *largest n.* By convention, the principle axis is in the . *This molecule and all square planar molecules have 4* σ_v





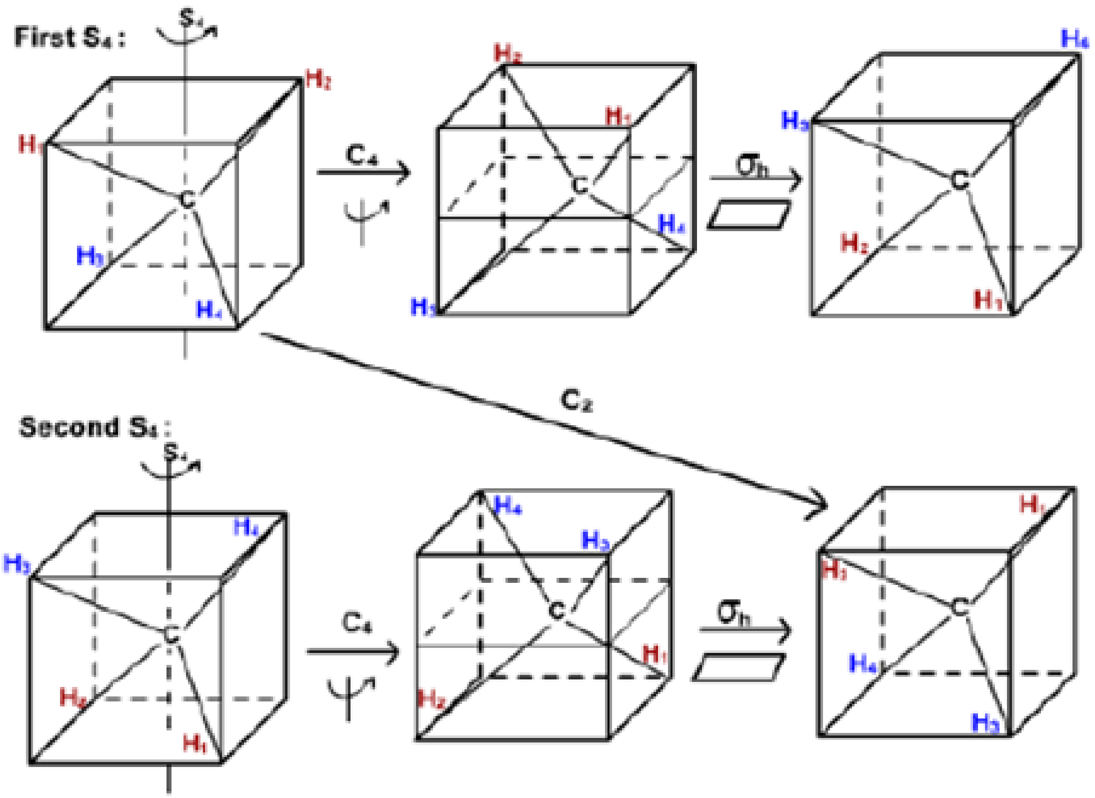


c-Trigonal molecules BCl_3 or BF_3 is a trigonal planar molecule. All trigonal planar molecules have a principal C_3 axis out of the page, three different C_2 axes, and three σ_v containing the principal axis



Rotation-reflection axis: an axis around which a rotation is followed by a reflection in a plane perpendicular to it, leaves the molecule unchanged. Also called an *n*-fold **improper rotation axis**, it is abbreviated S_n.

Rotation-reflection, Improper axis (S_n)



$2 S_4 = 1 C_2$

Rotation Angle	Symmetry Operation
90°	S_4
180°	C_2(=2S_4)Above example
270°	3S_4
360°	E(=4S4)

S_n (n even) Axis

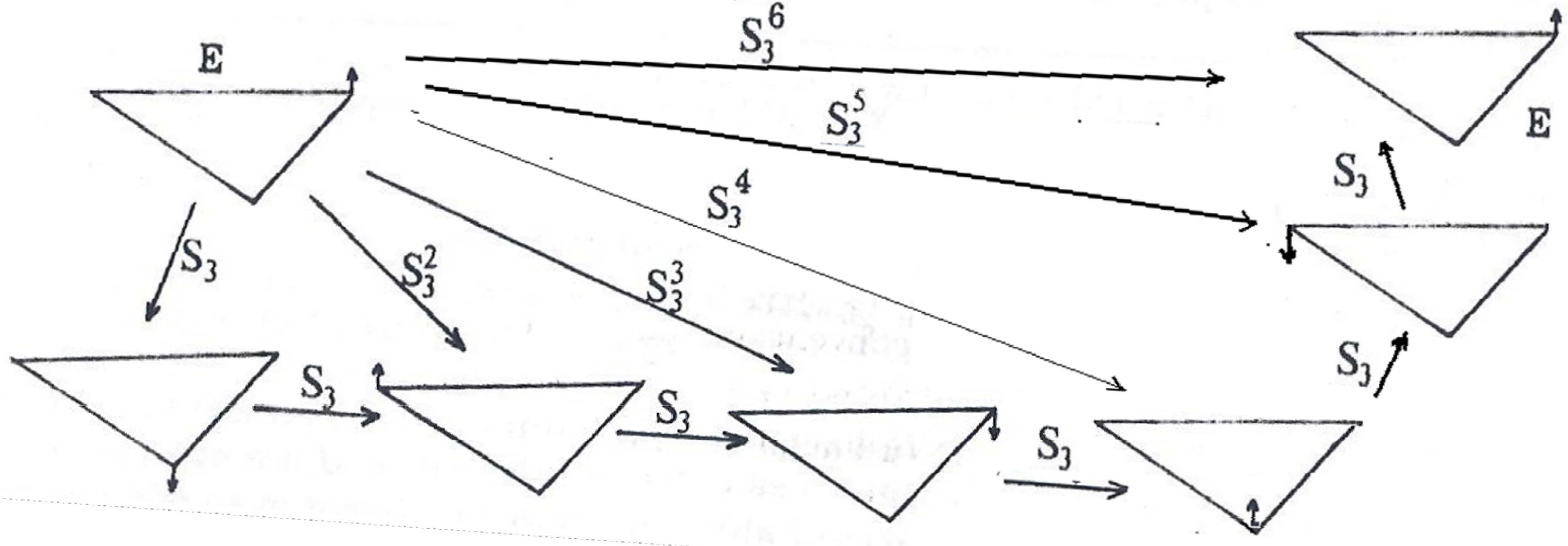
Generates n operations: S_n^1, S_n^2, ...S_n^{n-1}, S_n^n (= E)

$S_n^n = E$

S_n (n odd) Axis

Generates 2n operations: S_n^1, S_n^2, ...S_n^{2n-1}, S_n^{2n} (=E)

$S_n^{2n} = E$



for n odd $S_n^{2n} = E$

In contrast to S_6 and C_3, applying the operation n times, where n is the order of the axis does not bring us back to the identity.

For **n** even $S_n^{\ n} = E$

Inorganic Chemistry

Second year

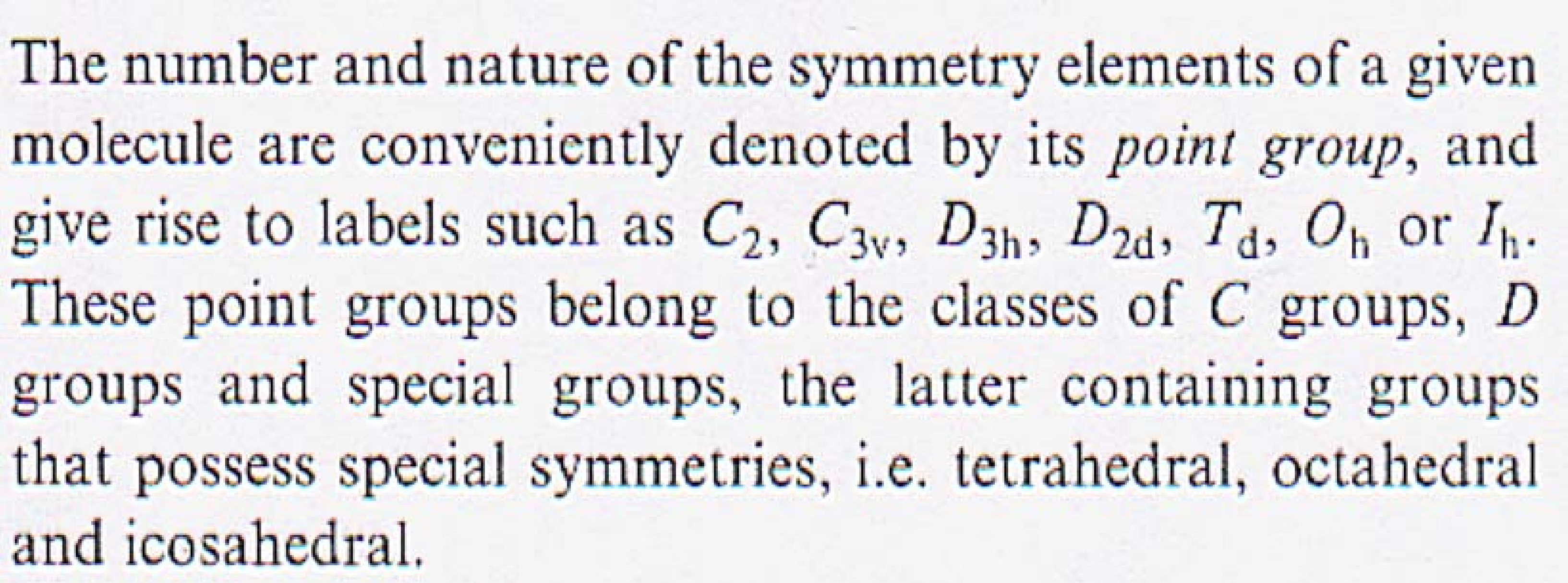
1st semester

LECTURE 10

Dr. Ahlam Jameel Abdul-Ghani

Dr. Asmaa Mohammed Noori Khaleel

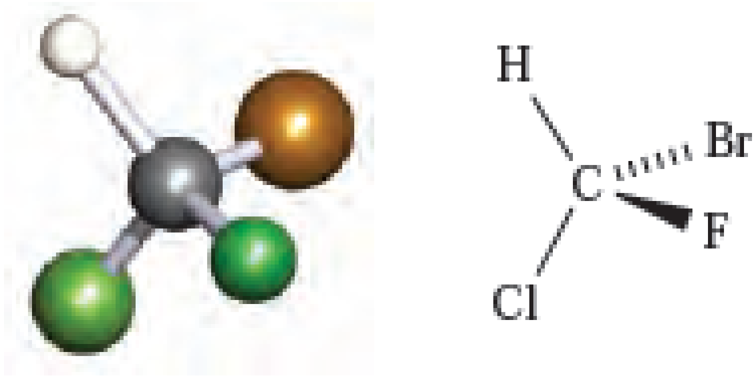
Point groups



The number and nature of the symmetry elements of a given molecule are conveniently denoted by its *point group*, and give rise to labels such as C_2, C_{3v}, D_{3h}, D_{2d}, T_d, O_h or I_h. These point groups belong to the classes of C groups, D groups and special groups, the latter containing groups that possess special symmetries, i.e. tetrahedral, octahedral and icosahedral.

C_1 point group

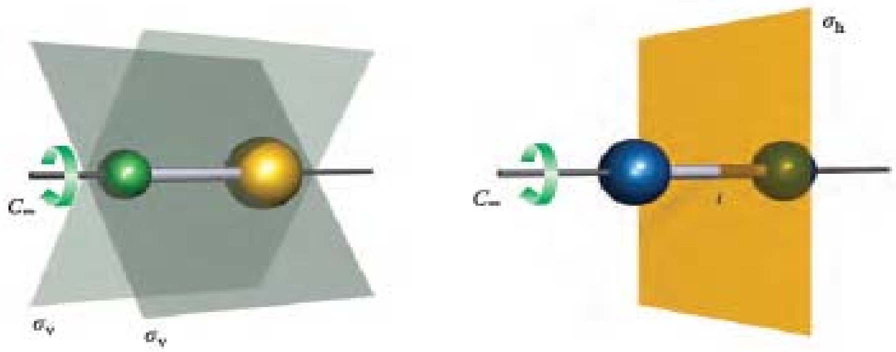
Molecules that appear to have no symmetry at all, e.g. **3.9**, must possess the symmetry element E and effectively possess at least one C_1 axis of rotation. They therefore belong to the C_1 point group, although since $C_1 = E$, the rotational symmetry operation is ignored when we list the symmetry elements of this point group.



(3.9)

$C_{\infty v}$ point group

C_∞ signifies the presence of an ∞-fold axis of rotation, i.e. that possessed by a linear molecule (Figure 3.7); for the molecular species to belong to the $C_{\infty v}$ point group, it must also possess an infinite number of σ_v planes but *no* σ_h plane or inversion centre. These criteria are met by asymmetrical diatomics such as HF, CO and $[CN]^-$ (Figure 3.7a).

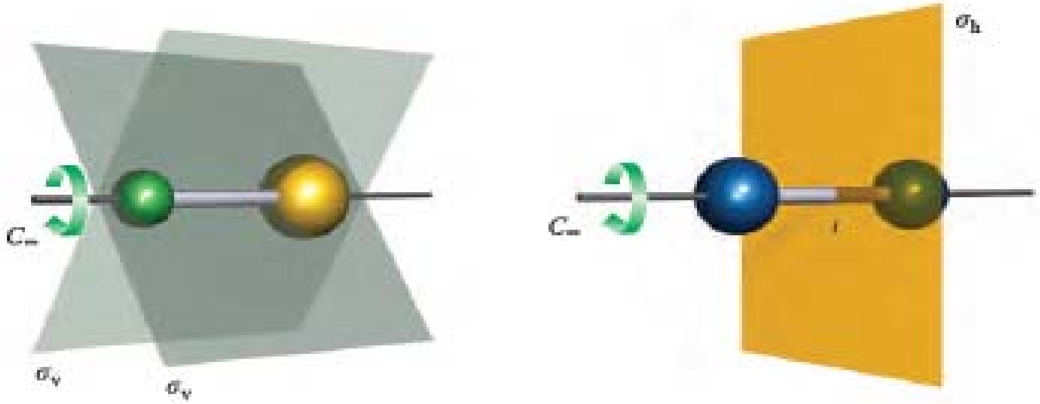


(a) (b)

Fig. 3.7 Linear molecular species can be classified according to whether they possess a centre of symmetry (inversion centre) or not. All linear species possess a C_∞ axis of rotation and an infinite number of σ_v planes; in (a), two such planes are shown and these planes are omitted from (b) for clarity. Diagram (a) shows an asymmetrical diatomic belonging to the point group $C_{\infty v}$, and (b) shows a symmetrical diatomic belonging to the point group $D_{\infty h}$.

$D_{\infty h}$ point group

Symmetrical diatomics (e.g. H_2, $[O_2]^{2-}$) and linear polyatomics that contain a centre of symmetry (e.g. $[N_3]^-$, CO_2, HC≡CH) possess a σ_h plane in addition to a C_∞ axis and an infinite number of σ_v planes (Figure 3.7). These species belong to the $D_{\infty h}$ point group.



(a) (b)

Fig. 3.7 Linear molecular species can be classified according to whether they possess a centre of symmetry (inversion centre) or not. All linear species possess a C_∞ axis of rotation and an infinite number of σ_v planes; in (a), two such planes are shown and these planes are omitted from (b) for clarity. Diagram (a) shows an asymmetrical diatomic belonging to the point group $C_{\infty v}$, and (b) shows a symmetrical diatomic belonging to the point group $D_{\infty h}$.

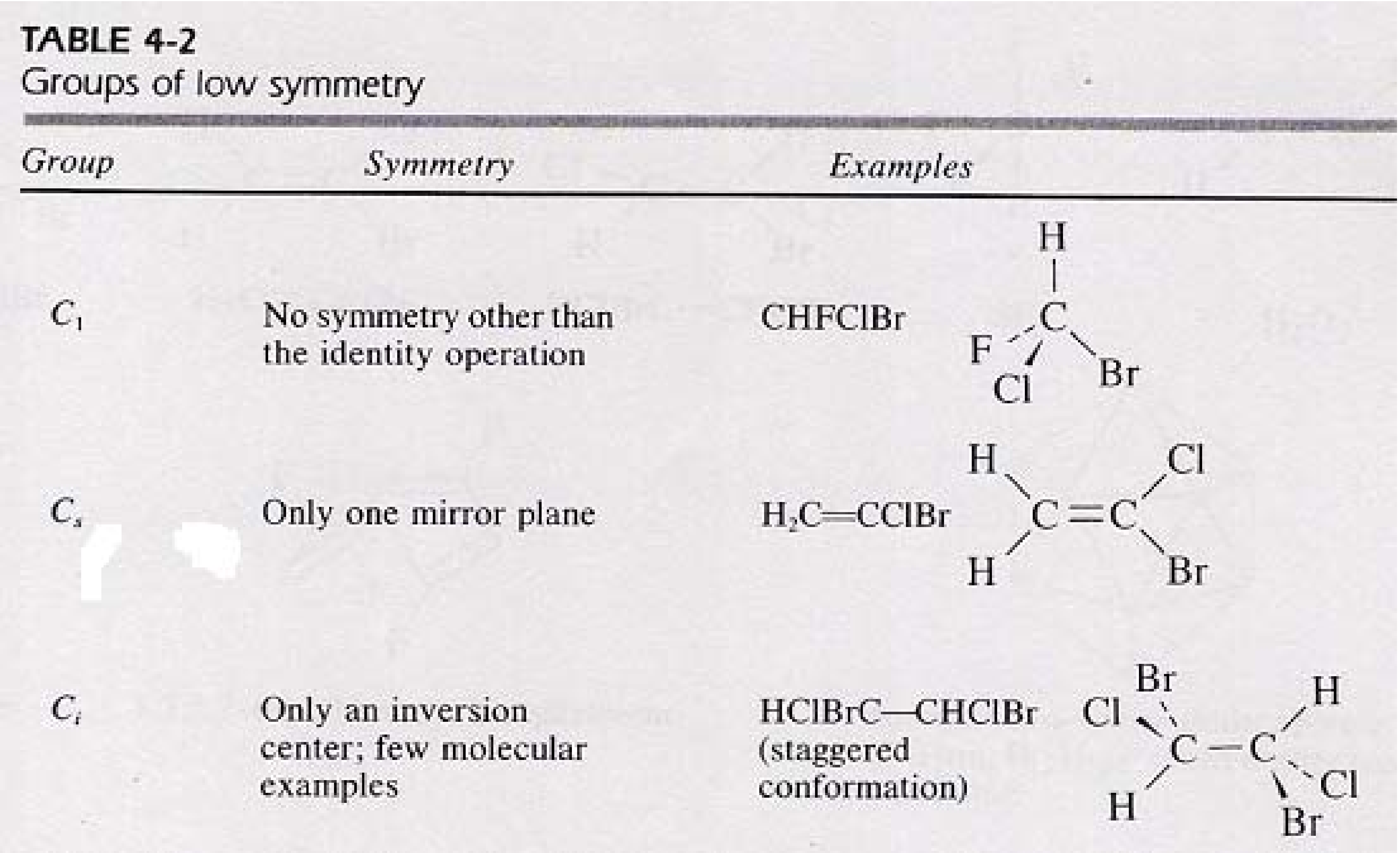


TABLE 4-2
Groups of low symmetry

Group	*Symmetry*	*Examples*
C_1	No symmetry other than the identity operation	CHFClBr
C_s	Only one mirror plane	$H_2C{=}CClBr$
C_i	Only an inversion center; few molecular examples	HClBrC—CHClBr (staggered conformation)

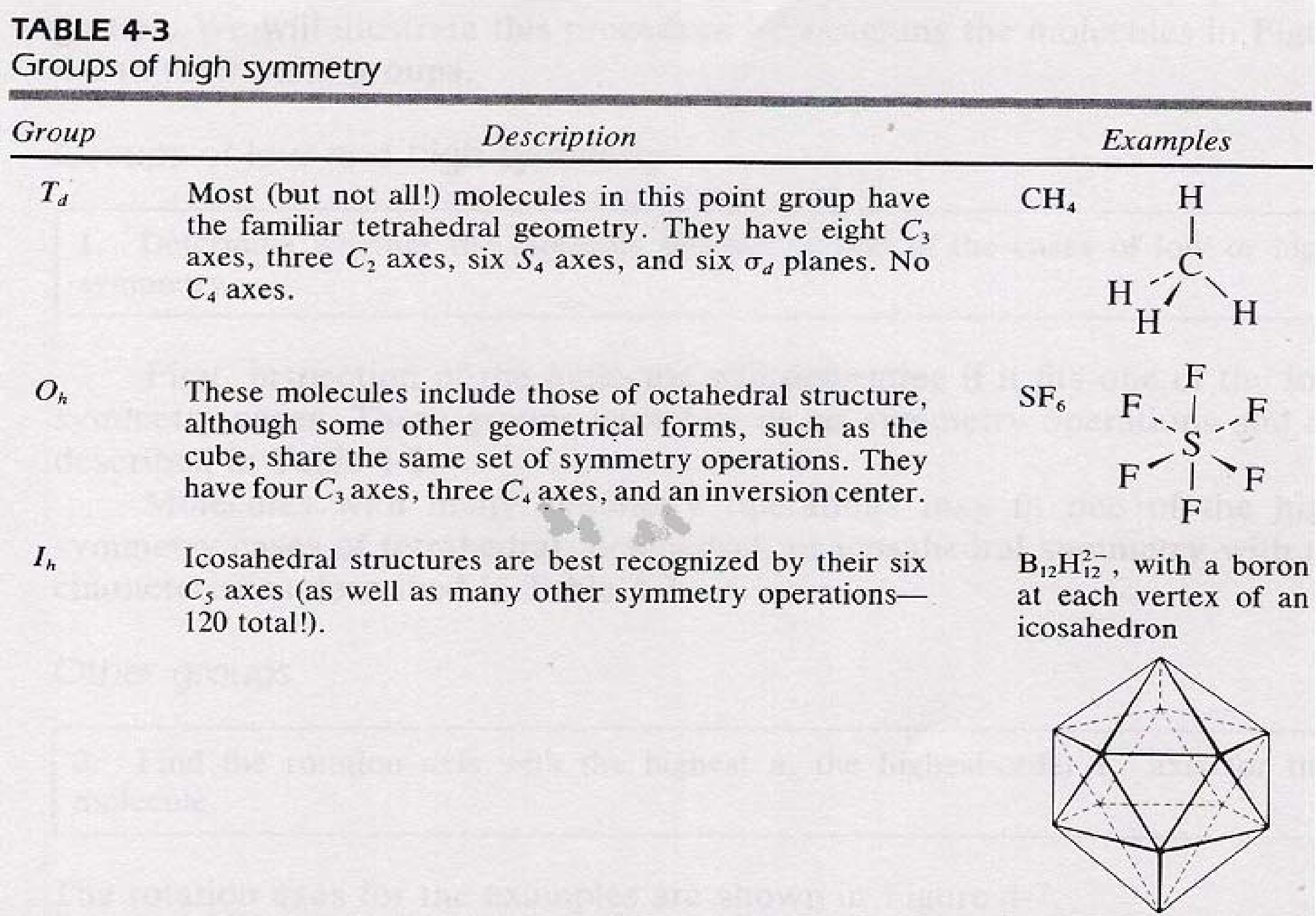
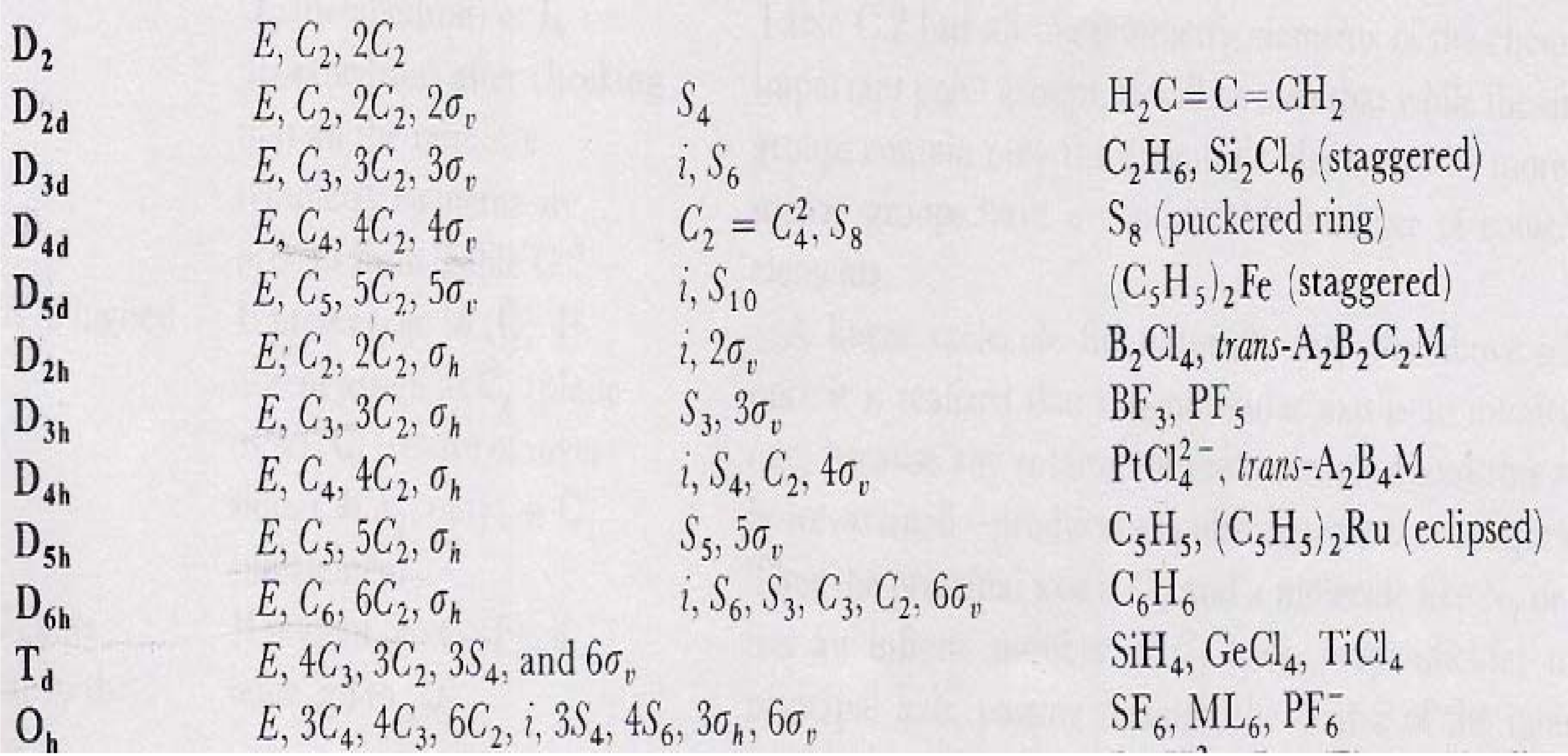


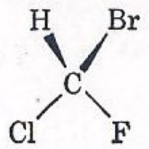
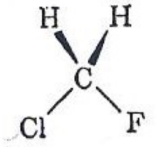
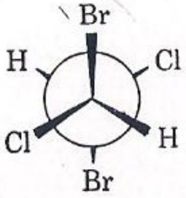
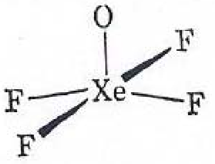
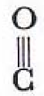
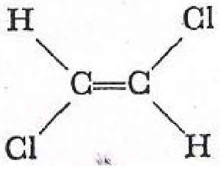
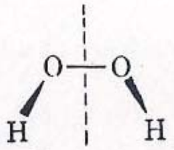
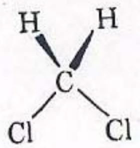
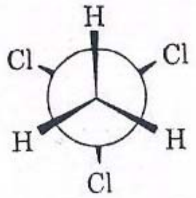
TABLE 4-3
Groups of high symmetry

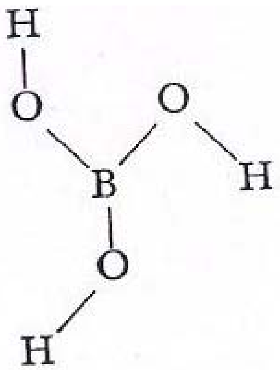
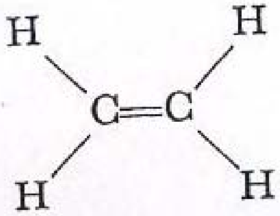
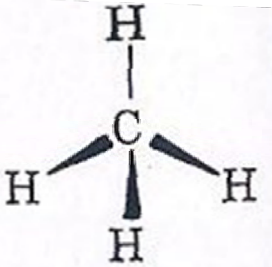
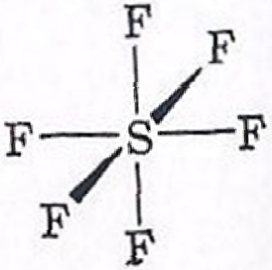
Group	*Description*	*Examples*
T_d	Most (but not all!) molecules in this point group have the familiar tetrahedral geometry. They have eight C_3 axes, three C_2 axes, six S_4 axes, and six σ_d planes. No C_4 axes.	CH_4
O_h	These molecules include those of octahedral structure, although some other geometrical forms, such as the cube, share the same set of symmetry operations. They have four C_3 axes, three C_4 axes, and an inversion center.	SF_6
I_h	Icosahedral structures are best recognized by their six C_5 axes (as well as many other symmetry operations—120 total!).	$B_{12}H_{12}^{2-}$, with a boron at each vertex of an icosahedron

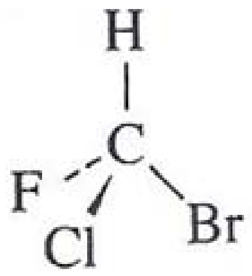
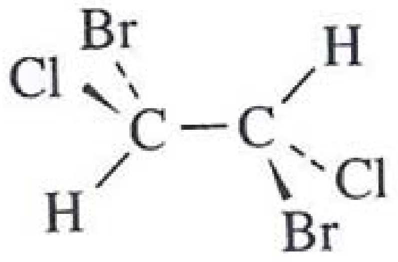
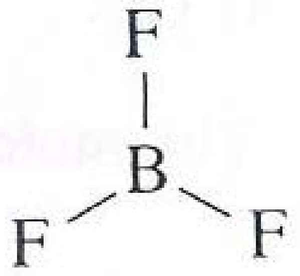
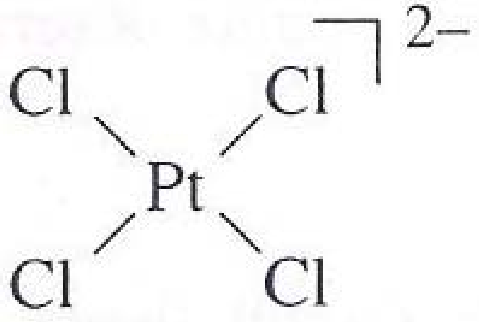
Point group	*Diagnostic elements*		*Examples*
$\mathbf{C_1}$	E only		SiHClBrI
$\mathbf{C_s}$	E, σ only		SiH_2ClBr
$\mathbf{C_i}$	E, i only		*trans*-HClBrSiSiBrClH
$\mathbf{C_2}$	E, C_2 only		H_2O_2 (non-planar)
$\mathbf{C_{2v}}$	$E, C_2, 2\sigma_v$		H_2O, SiH_2Cl_2
$\mathbf{C_{3v}}$	$E, C_3, 3\sigma_v$		NH_3, $SiHCl_3$
$\mathbf{C_{4v}}$	$E, C_4, 4\sigma_v$	$C_2 = C_4^2$	BrF_5, SF_5Cl
$\mathbf{C_{2h}}$	E, C_2, σ_h	i	*trans*-$C_6H_2Cl_2Br_2$



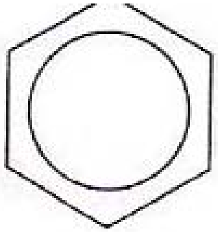
D_2	$E, C_2, 2C_2$		
D_{2d}	$E, C_2, 2C_2, 2\sigma_v$	S_4	$H_2C=C=CH_2$
D_{3d}	$E, C_3, 3C_2, 3\sigma_v$	i, S_6	C_2H_6, Si_2Cl_6 (staggered)
D_{4d}	$E, C_4, 4C_2, 4\sigma_v$	$C_2 = C_4^2, S_8$	S_8 (puckered ring)
D_{5d}	$E, C_5, 5C_2, 5\sigma_v$	i, S_{10}	$(C_5H_5)_2Fe$ (staggered)
D_{2h}	$E, C_2, 2C_2, \sigma_h$	$i, 2\sigma_v$	B_2Cl_4, *trans*-$A_2B_2C_2M$
D_{3h}	$E, C_3, 3C_2, \sigma_h$	$S_3, 3\sigma_v$	BF_3, PF_5
D_{4h}	$E, C_4, 4C_2, \sigma_h$	$i, S_4, C_2, 4\sigma_v$	$PtCl_4^{2-}$, *trans*-A_2B_4M
D_{5h}	$E, C_5, 5C_2, \sigma_h$	$S_5, 5\sigma_v$	C_5H_5, $(C_5H_5)_2Ru$ (eclipsed)
D_{6h}	$E, C_6, 6C_2, \sigma_h$	$i, S_6, S_3, C_3, C_2, 6\sigma_v$	C_6H_6
T_d	$E, 4C_3, 3C_2, 3S_4$, and $6\sigma_v$		SiH_4, $GeCl_4$, $TiCl_4$
O_h	$E, 3C_4, 4C_3, 6C_2, i, 3S_4, 4S_6, 3\sigma_h, 6\sigma_v$		SF_6, ML_6, PF_6^-

Schoenflies Symbol	Symmetry Elements	Molecular Configuration
C_1	E	
C_s	E, σ	
C_i	E, i	
C_{4v}	$E, C_4(C_2), 4\sigma_v$	
$C_{\infty v}$	$E, C_\infty, \infty\sigma_v$	
C_{2h}	E, C_2, σ_h, i	
C_2	E, C_2	
C_{2v}	$E, C_2, 2\sigma_v$	
C_{3v}	$E, C_3, 3\sigma_v$	

$\boldsymbol{C_{3h}}$	$E, C_3(S_3), \sigma_h$	
$\boldsymbol{D_{2h}}$	$E, C_2, 2C_2, \sigma_h, 2\sigma_v, i$	
$\boldsymbol{T_d}$	$E, 3C_2(3S_2), 4C_3, 6\sigma_d$	
$\boldsymbol{O_h}$	$E, 3C_4(3C_2, 3S_4),$ $4C_2(4S_6), 3\sigma_h 6C_2,$ $6\sigma_d, i$	

C_1	No symmetry other than the identity operation	CHFClBr	
C_i	Only an inversion center; few molecular examples	HClBrC—CHClBr (staggered conformation)	
D_{nh}	D_{3h}	$\mathrm{BF_3}$	
	D_{4h}	$\mathrm{PtCl_4^{2-}}$	

D_{6h} benzene



$D_{\infty h}$ F_2, N_2, $F-F$ $N\equiv N$

acetylene (C_2H_2) $H-C\equiv C-H$

D_{nd}

D_{2d} allene ($H_2C{=}C{=}CH_2$)