

Fillet of a fenny snake, Into the cauldron boil and bake

# **5. ELECTROACTIVE ORGANIC COMPOUNDS**

Source  
No Spec: Text  
W: Wikipedia

# Contents

- Chemistry Essentials
- Overview of Structures and Fundamental Properties
  - Conductive Polymers
  - Charge-Transfer Complexes
  - Buckyballs and Nanotubes
- Piezoelectricity, Pyroelectricity, and Ferroelectricity
  - Basic Principles
  - Organic Materials System
- Magnetism
  - Basic Principles
  - Organic Magnets

# Moles and Molecules

- One mole refers to the amount of substance consisting of  $6.02 \times 10^{23}$  ( $N_A$ , Avogadro number) elementary entities
- 1 mole of C weighs 12 g
- 1 mole of gas takes the same volume of 22.4 L regardless of their chemical nature.
- Number of molecules per unit volume ( $n$ ) is given as

$$n = \frac{N_A \rho}{M} \quad , \text{where } \rho \text{ is density, } M \text{ is molecular weight}$$

- Gas const (R) and Boltzmann const

$$R = k_B N_A$$

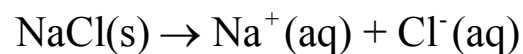
$$R = 8.314472 \text{ JK}^{-1}\text{M}^{-1}$$

$$k_B = 1.3806504 \times 10^{-23} \text{ JK}^{-1}$$

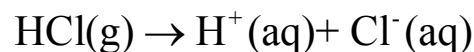
# Acids and Bases

- 1884 **Arrhenius** : ions in water  
Acid: H<sup>+</sup> generation when dissolved in water (HCl etc)  
Base: OH<sup>-</sup> generation when dissolved in water (NaOH etc)
- 1923 **Lowry & Brönsted**  
Acid: H<sup>+</sup> donor  
Base: H<sup>+</sup> acceptor (NH<sub>3</sub> etc)
- 1923 Gilbert **Lewis**  
Acid: electron acceptor  
Base: electron donor
- **pH = -log[H<sup>+</sup>]**  
pH=7 for water, [H<sup>+</sup>] is 1.0 x 10<sup>-7</sup> mol L<sup>-1</sup>  
Acids: pH <7  
Base: pH >7  
Doubled [H<sup>+</sup>] lowers pH by 0.3

## Ionization



## Arrhenius Acid



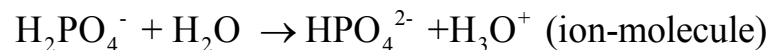
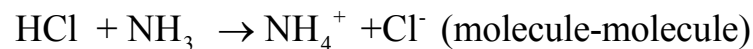
## Broensted Base but not the Arrhenius Base:



## Lewis Acid but not the Broensted Acid:

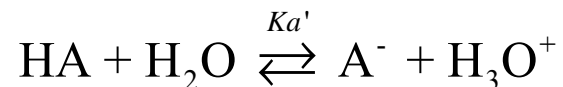


acid    base



*What about the position of equilibrium?*

# Acidity Constant (pKa)



$$K_a' = \frac{[\text{A}^-][\text{H}_3\text{O}^+]}{[\text{HA}][\text{H}_2\text{O}]} \quad \text{and} \quad [\text{H}_2\text{O}] = 55.4 \text{ mol L}^{-1}$$

$$-\Delta G^0 = RT \ln K$$

We write the above equation in short for convenience

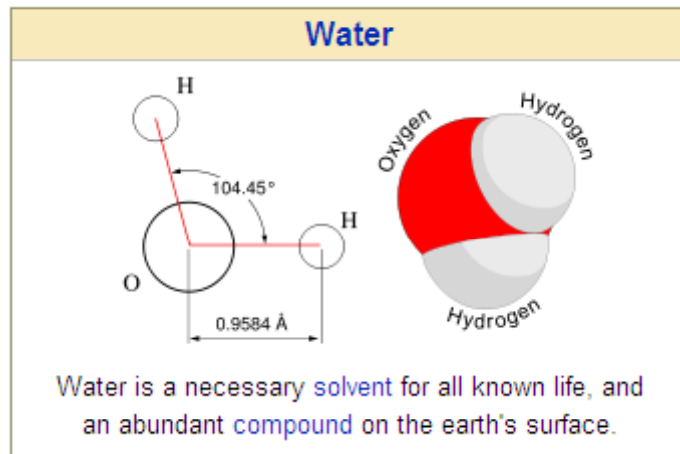


$$\text{pKa} = -\log_{10} K_a$$

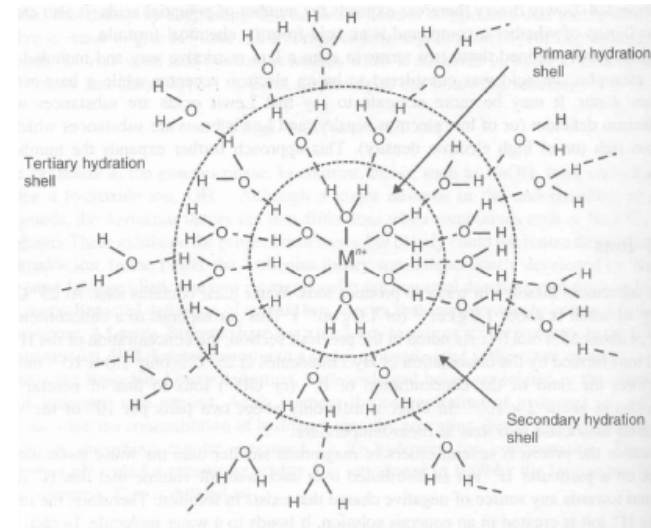
Compound	Equilibrium	pK <sub>a</sub>	ΔH <sup>θ</sup> /kJ mol <sup>-1</sup>	-TΔS <sup>θ</sup> /kJ mol <sup>-1</sup>
HA = Acetic acid	HA ⇌ H <sup>+</sup> + A <sup>-</sup>	4.756	-0.41	27.56

# Ions

- Water: density  $\sim 1.0 \text{ g cm}^{-3}$ ,  $[\text{H}_2\text{O}] = 55.4 \text{ mol L}^{-1}$ , self-ionization  $1.0 \times 10^{-7} \text{ mol L}^{-1} \rightarrow [\text{H}_3\text{O}^+]/[\text{H}_2\text{O}] = 2 \times 10^{-9}$
- **Proton** is several orders of magnitude smaller than the water molecule, thus attracted immediately to water molecules and surrounded by them (usu. 4):  $\text{H}(\text{H}_2\text{O})_4^+$
- **Ions** dissolved in water forms **hydration shell** and weaken the structure of H-bonding of water  $\rightarrow$  lowers the  $T_m$ ; freezing point depression  $\rightarrow$  Salt water has a lower freezing point than water
- Water is polar ( $\epsilon = 78$ ) H-bond forming solvent






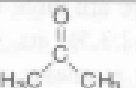
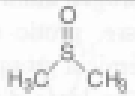
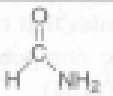
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# Solvents

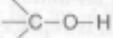
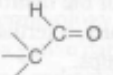
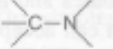
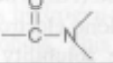
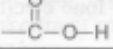
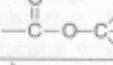
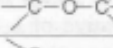
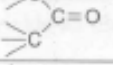
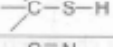

- Thermodynamics of solution:  
'like dissolves like';  $\Delta G = \Delta H - T\Delta S$
- Why solvents?  
Processing to the required shape  
Facilitate the reaction; more collision via solvation and heat dissipation
- **Polar & Nonpolar** Solvents:  
Dipole moment, Dielectric constant, Miscibility with water
- **Protic & Aprotic** solvents
- (Note the smallest size of proton; stronger Coulomb interaction)

Table 5.1 Properties of some common organic solvents.

Solvent	Structure	Boiling point (°C)	Dielectric constant	Class	
				Polar	Protic
Hexane	$\text{CH}_3(\text{CH}_2)_4\text{CH}_3$	69	2		
Benzene		80	2.3		
Diethyl ether	$\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$	35	4.3		
Chloroform	$\text{CHCl}_3$	61	4.8		
Acetic acid		118	6.1	*	*
Tetrahydrofuran (THF)		66	7.6		
Acetone		56	21	*	
1-Propanol	$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	97	20	*	*
Ethanol	$\text{CH}_3\text{CH}_2\text{OH}$	78	25	*	*
Methanol	$\text{CH}_3\text{OH}$	65	33	*	*
Acetonitrile	$\text{H}_3\text{CC}\equiv\text{N}$	82	38	*	
Dimethyl sulfoxide (DMSO)		189	47	*	
Water	$\text{H}-\text{O}-\text{H}$	100	78	*	*
Formamide		210	111	*	*

# Functional Groups

Table 5.2 Chemical structures of common functional groups found in organic compounds.

Compound type	Functional group
Alcohol	
Aldehyde	
Amine	
Amide	
Carboxylic acid	
Ester	
Ether	
Ketone	
Thiol	
Nitrile	

- **Alcohol**(R-OH): polar, protic, solubility in water (depends on R), forms alkoxide base RO<sup>-</sup>M<sup>+</sup> with reactive metal or NaH
- **Aldehyde**: polar, E<sup>+</sup> center (C=O)
- **Amines**: unshared pair of electrons, organic base, H-bonding, primary to tertiary amines
- **Amides**: carboxylic acid derivative
- **Carboxylic acid**: acidity, pKa=4.76 for acetic acid (0.02% ionized in water).
- **Esters**: H-bond acceptor but not donor, distinctive odors- artificial flavouring and fragrances
- **Ethers**: H-bond acceptor but weaker, low boiling point, anesthesia
- **Ketones**: polar, acetone is most common solvent
- **Thiols**: mercaptan, strong odour, special binding to Au surface
- **Nitrile**: polar, electron withdrawing



# Aromatic Compound

- Benzene & fused benzene rings derivative, Heteroaromatic compounds
- Aroma, Aromatic stabilization energy, substitution reaction rather than addition
- Huckel rule: delocalized  $\pi$ -electron system, planar,  $4n+2$  electrons
- Five and six membered heteroaromatic rings: different use of unshared electrons; basicity and electron density in the ring
- Most important molecules for 'Molecular Electronics'

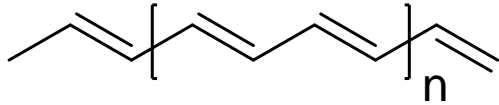
Chemical compound		Chemical compound	
Anthracene		Benzo[a]pyrene	
Chrysene		Coronene	
Corannulene		Naphthalene	
Naphthalene		Pentacene	
Phenanthrene		Pyrene	
Triphenylene		Ovalene	

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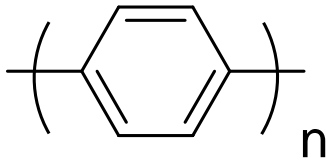
Table 5.3 Example of aromatic molecules containing heteroatoms.

Molecule	Structure	Molecule	Structure
Pyridine		Indole	
Pyrazine		Purine	
Pyrimidine		Furan	
Thiophene		Oxazole	
Pyrrole		Thiazole	

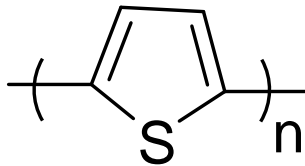
# Conjugated Polymers



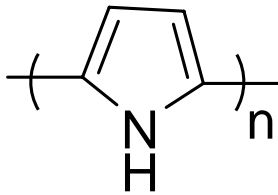
Polyacetylene (PA)



Poly-p-phenylene (PPP)



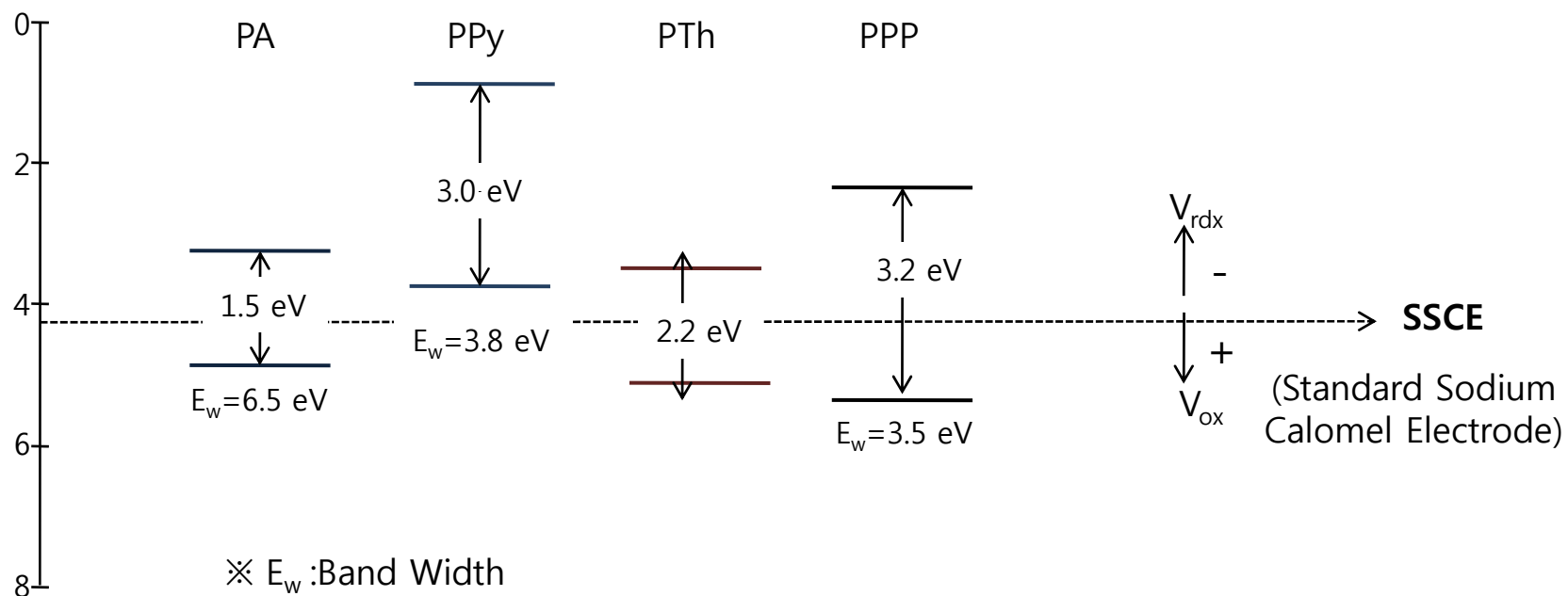
Polythiophene (PTh)



Polypyrrole (PPy)

## Electronic Parameters (PA,Ppy,PPP\*)

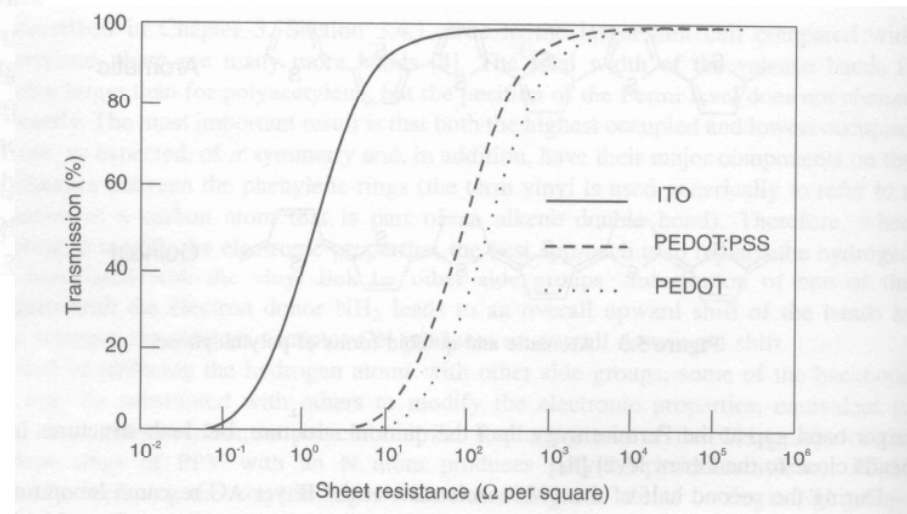
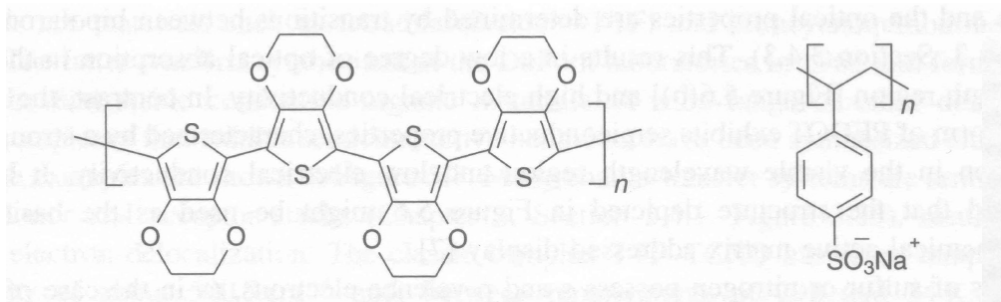
	$I_p(\text{eJ})$	$E.A.(\text{eJ})$	$E_g(\text{eV})$	$V_{\text{ox}}$	$V_{\text{rdx}}$
PA	4.7	3.2	1.5	0.4	-1.1
PPy	3.8	0.8	3.0	-0.6	-3.6
PPP	5.6	2.3	3.3	1.2	-2.1
PTh			2.2	1.1	



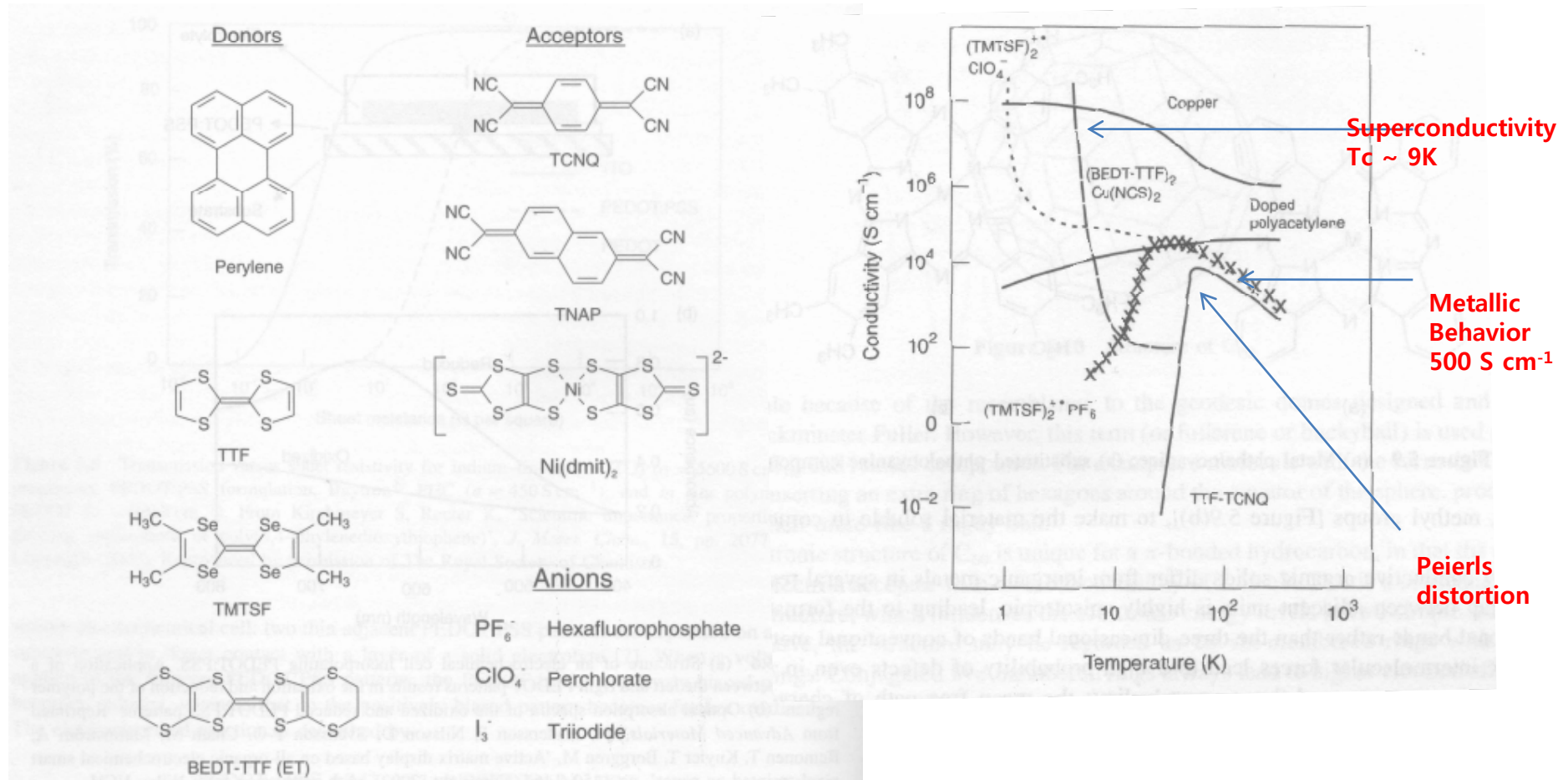


# PEDOT:PSS Transparent Conducting Polymer

- Poly(3,4-ethylenedioxythiophene): insoluble polymer, transparent and stable in oxidized state
- PEDOT:PSS is water soluble complex
- Potential application: capacitors, antistatic coating, printed circuit board, semi-transparent electrode for OLED
- Shows electrochromic properties (Fig 5.6)



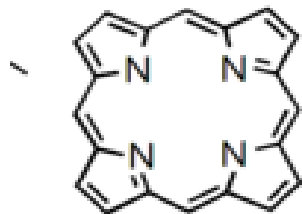
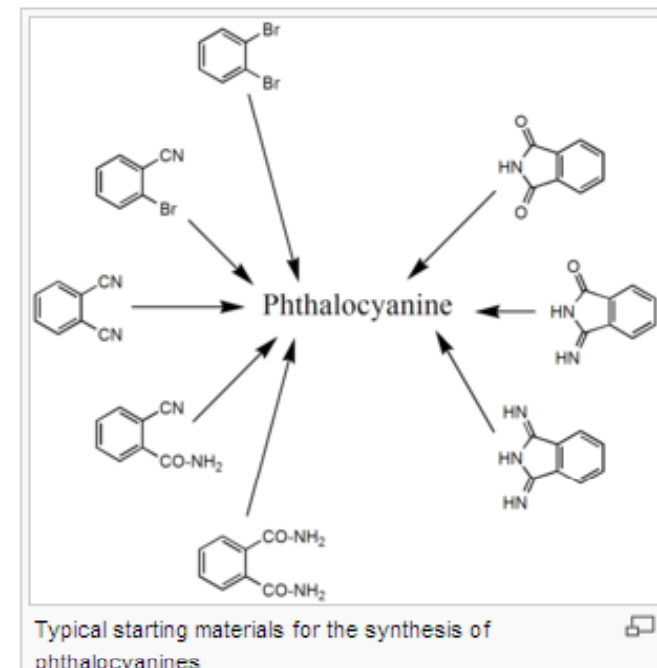
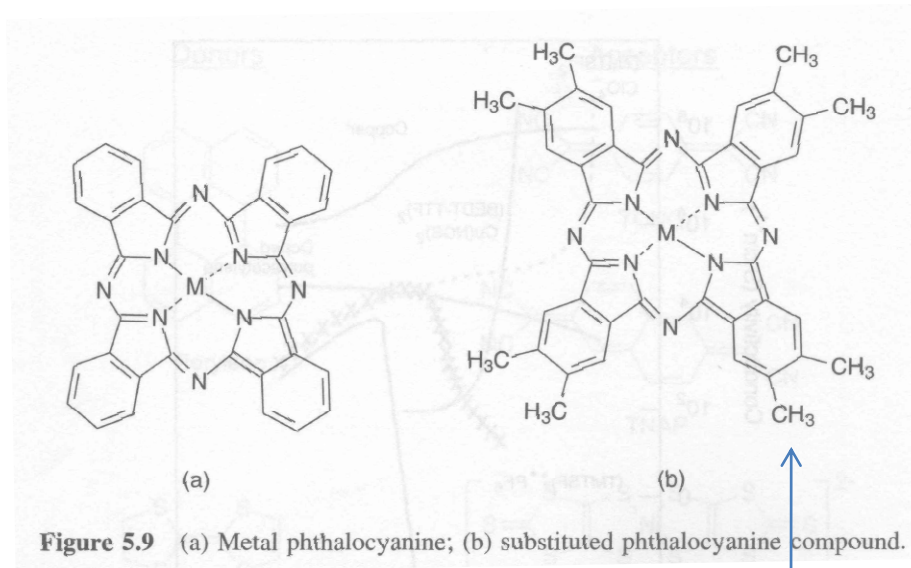
# CT Complexes



**Figure 5.7** Examples of compounds that can form charge-transfer complexes. Electron donors are shown on the left: perylene, tetrathiafulvalene (TTF), tetramethyltetraselenafulvalene (TMTSF) and bis(ethylenedithio)-TTF (BEDT-TTF or ET). Electron acceptors and anions are shown on the right: tetracyanoquinodimethane (TCNQ), tetracyanonaphthalene (TNAP) and Ni(dmit)<sub>2</sub> (H<sub>2</sub>dmit = 4,5-dimercapto-1,3-dithiole-2-thione).

# Phthalocyanines

- Becomes electrically conductive on oxidation ( $I_2$ ,  $Br_2$  etc):  
Hosts various transition metals (M=Fe, Cu, Co, Ni, Zn)

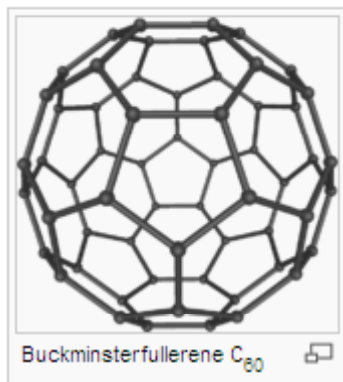


Porphyrin

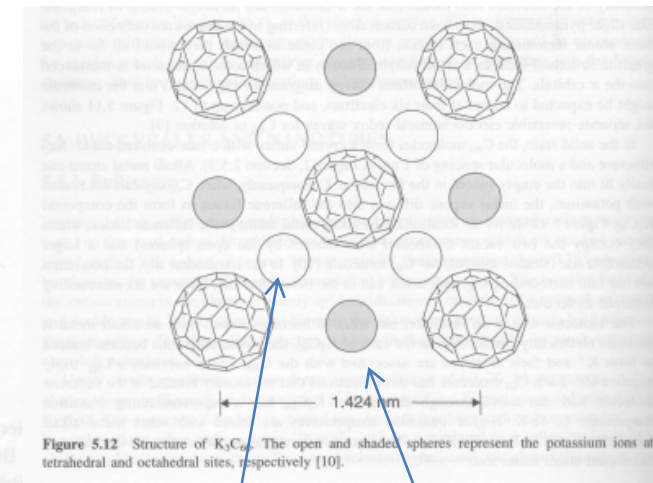
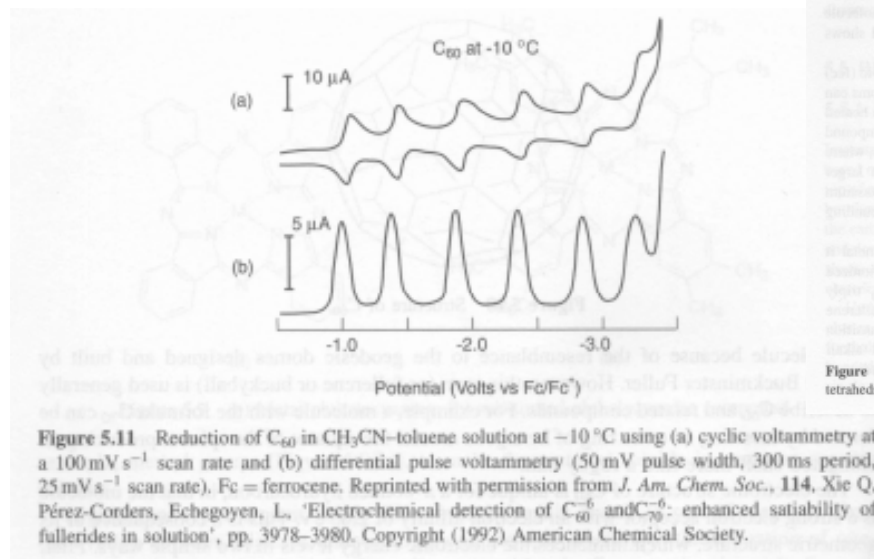
Methyl substitutions gives solubility

# Fullerenes : C<sub>60</sub>

- Discovered in 1985 by Kroto, Curl, and Smalley (1996 Nobel prize in chemistry)
- Diameter is about 1 nm. Comprises 20 hexagones and 12 pentagones
- 5-membered conjugated rings are source of electron affinity: to make cyclopentadienyl anion.
- Good electron acceptor; at least 6 electrons and possibly up to 12 electrons
- Doped C60 with potassium metal: K<sub>3</sub>C<sub>60</sub> is a conductor and shows super conductivity at below 18 K



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Tetrahedral site

Octahedral site

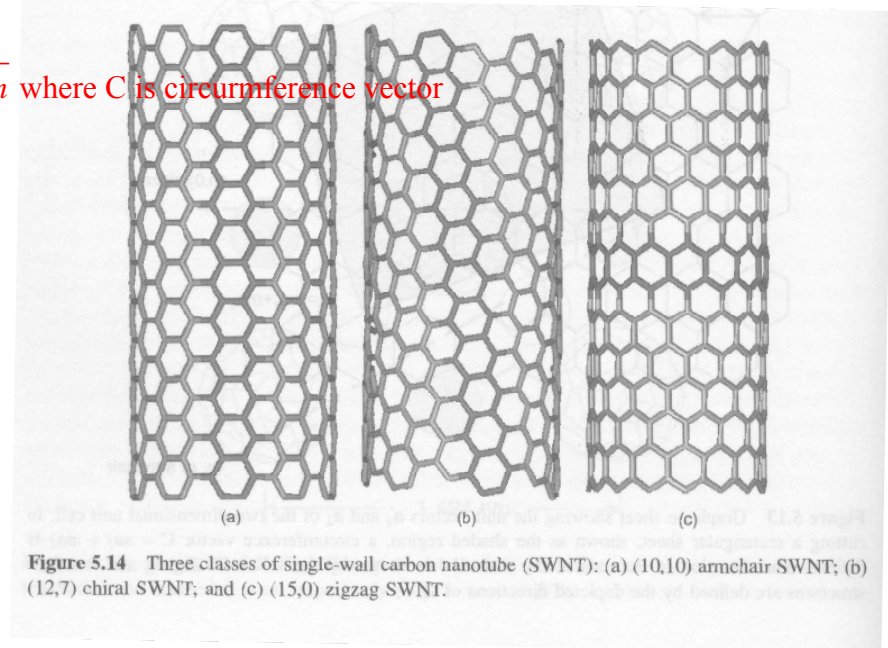
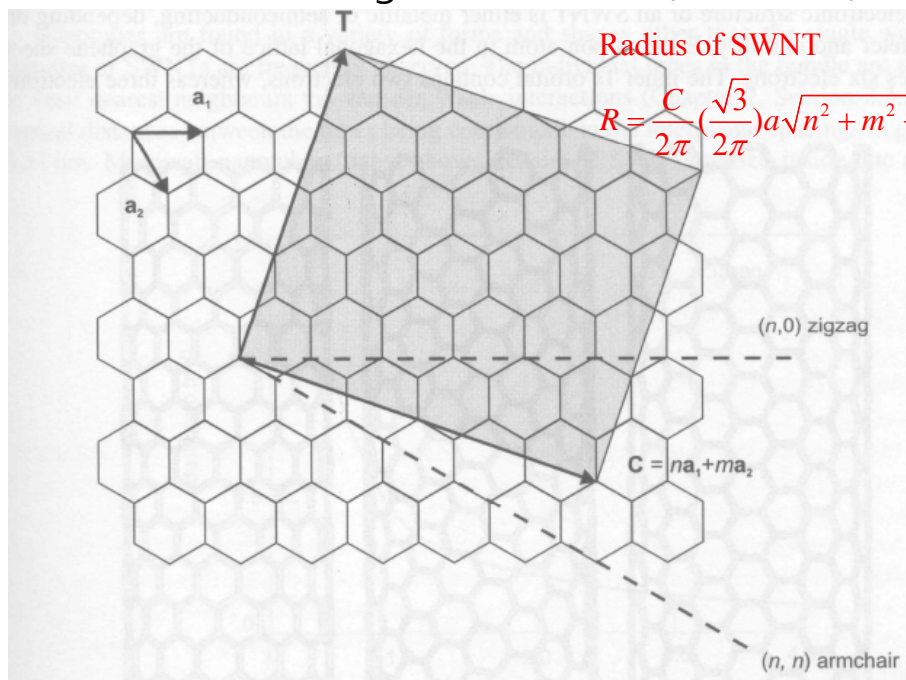




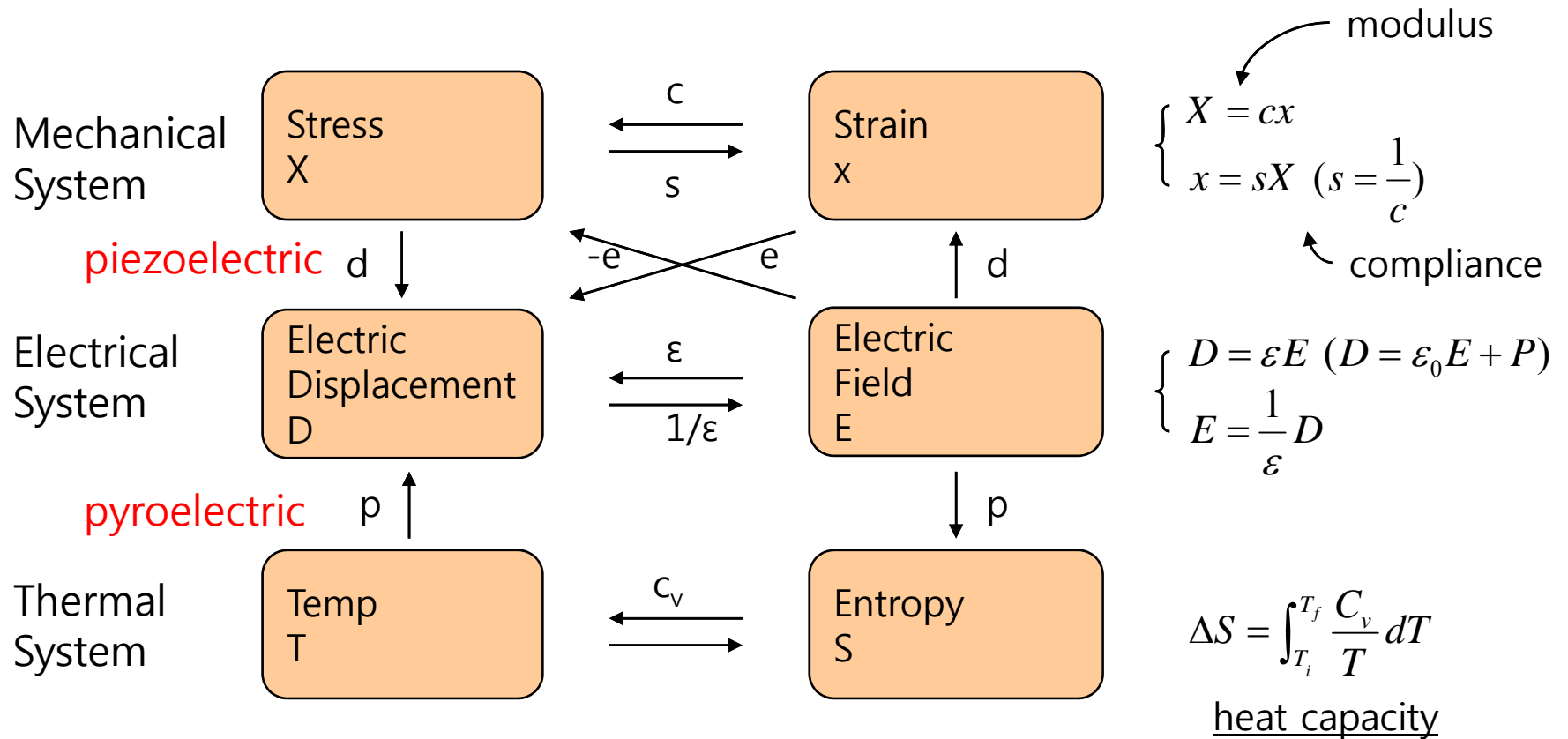
Nanotubes being grown by plasma enhanced chemical vapor deposition

# Carbon Nanotubes (CNT)

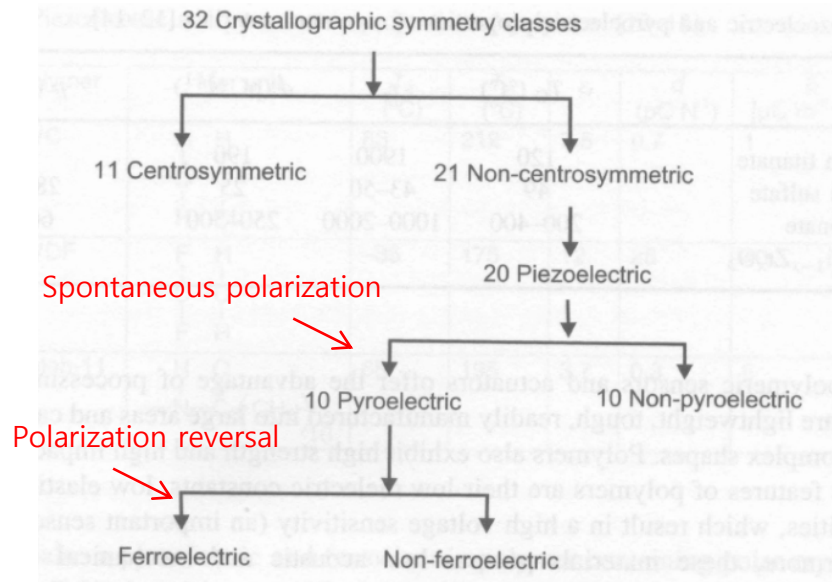
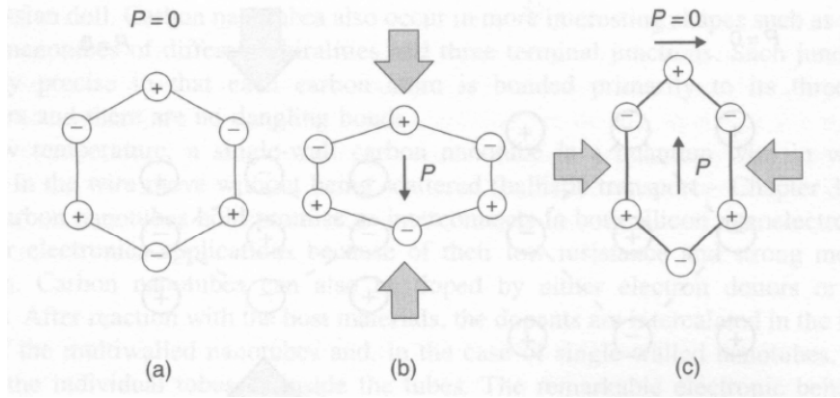
- 1991 Sumio Iijima at NEC discovered CNT
- Synthesized initially by arc discharge but since 1993 by PECVD
- Diameter down to 0.7 nm, metallic or semiconducting properties with doping capability and excellent mechanical properties
- Achiral SWNT: armchair (n,n) and zigzag (n,0), Chiral SWNT: others
- Metallic when  $|n-m| = 3I$  (I is an integer)
- Semiconducting with  $E_g = 0.45/R$  eV (where R is the radius of chiral SWNT)
- Multiwall nanotube: structured like Russian doll
- Tensile strength  $45 \times 10^9$  Pa (20 x steel), Young's modulus  $(1.3- 1.8) \times 10^9$  Pa (10x steel)



# Piezo-, Pyro-, and Ferroelectric



Piezoelectric : pressure-induced dipole moment



**Table 5.5** Piezoelectric and pyroelectric properties of common materials [12–14].

Material	$T_C$ ( $^{\circ}\text{C}$ )	$\epsilon_r$	$d$ ( $\text{pC N}^{-1}$ )	$p$ ( $\mu\text{C m}^{-2} \text{K}^{-1}$ )
BaTiO <sub>3</sub> , barium titanate	120	1900	190	200
TGS, triglycine sulfate	49	43–50	25	280–350
PZT, lead zirconate titanate, PbTi <sub>1-x</sub> Zr <sub>x</sub> O <sub>3</sub>	200–400	1000–2000	250–500	60–500

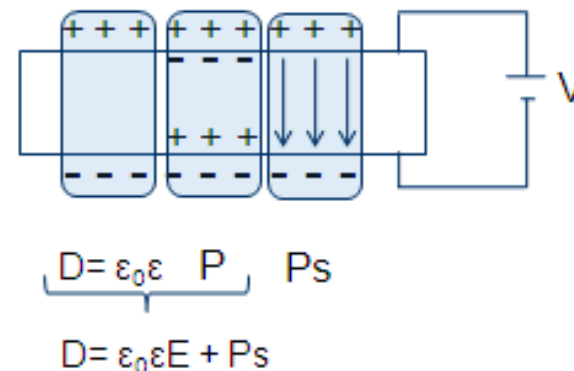
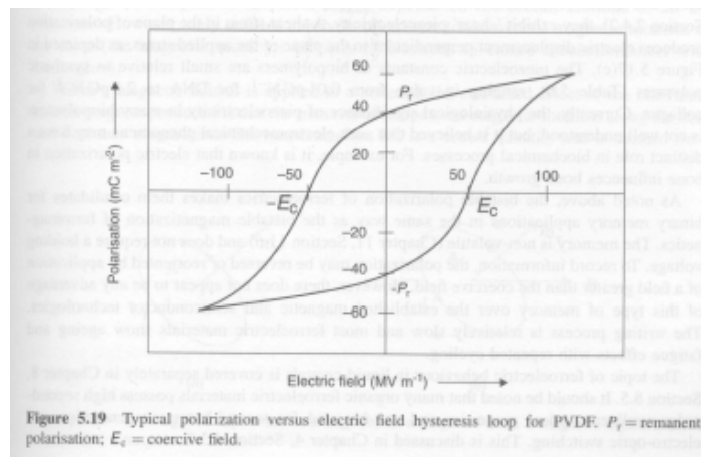
**Table 5.6** Piezoelectric and pyroelectric properties of polymers [12–14].

Polymer	Mer unit	$T_g$ ( $^{\circ}\text{C}$ )	$T_m$ ( $^{\circ}\text{C}$ )	$\epsilon_r$	$d$ ( $\text{pC N}^{-1}$ )	$p$ ( $\mu\text{C m}^{-2} \text{K}^{-1}$ )
PVC	$\begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ -\text{C}-\text{C}- \\   \quad   \\ \text{H} \quad \text{Cl} \end{array}$	83	212	3.5	0.7	1
PVDF	$\begin{array}{c} \text{F} \quad \text{H} \\   \quad   \\ -\text{C}-\text{C}- \\   \quad   \\ \text{F} \quad \text{H} \end{array}$	-35	175	12	28	40
Nylon-11	$\begin{array}{c} \text{H} \quad \text{O} \\   \quad    \\ -\text{N}-\text{C}-(\text{CH}_2)_{10} \end{array}$	68	195	3.7	0.3	5

# PVDF and Copolymers

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- PVDF is typically 50-60% crystalline. To give the material its piezoelectric properties, it is mechanically stretched to orient the molecular chains and then poled under tension. PVDF exists in several forms: alpha (TG<sup>+</sup>G<sup>-</sup>), beta (TTTT), and gamma (TTTGT<sup>+</sup>TTG<sup>-</sup>) phases, depending on the chain conformations as trans (T) or gauche (G) linkages. When poled, PVDF is a ferroelectric polymer, exhibiting efficient piezoelectric and pyroelectric properties. These characteristics make it useful in sensor and battery applications. Thin films of PVDF are used in some newer thermal camera sensors.
- Unlike other popular piezoelectric materials, such as PZT, PVDF has a negative  $d_{33}$  value. Physically, this means that PVDF will compress instead of expand or vice versa when exposed to the same electric field.
- Copolymers of PVDF are also used in piezoelectric and electrostrictive applications. One of the most commonly-used copolymers is P(VDF-TrFE), usually available in ratios of about 50:50 wt% and 65:35 wt% (equivalent to about 56:44 mol% and 70:30 mol%). Another one is P(VDF-TFE). They improve the piezoelectric response by improving the crystallinity of the material.
- While the copolymers' unit structures are less polar than that of pure PVDF, the copolymers typically have a much higher crystallinity. This results in a larger piezoelectric response.  $d_{33}$  values for P(VDF-TrFE) have been recorded to be as high as  $-38 \text{ pC/N}^7$  versus  $-33 \text{ pC/N}$  in pure PVDF<sup>5</sup>.



# Magnetic Properties

Magnetic dipole moment ( $\mathbf{m}_m$ )

$$\mathbf{m}_m = IA\mathbf{u}_n$$

\*1)  $\mathbf{m}_m$  of pairs of electrons in closed subshell cancel each other

thus only unfilled subshells contribute to the  $\mathbf{m}_{\text{atom}}$

$\mathbf{M}$  (magnetization;  $\text{Am}^{-1}$ ) = magnetic dipole moment per unit volume

$\mathbf{H}$  (magnetizing field;  $\text{Am}^{-1}$ ) = total field that would be present if the field were in vacuum

$\mathbf{B}$  (magnetic field: T) = total flux magnetic field lines through a unit crosssectional area of material

$$\mathbf{B} = \mu_0(\mathbf{H} + \mathbf{M}) \quad \text{and also} \quad \mathbf{B} = \mu_r \mu_0 \mathbf{H}$$

where  $\mu_0$  is the permeability of free space ( $4\pi \times 10^{-7} \text{ Hm}^{-1}$ ),  $\hat{\mu}_r$  is relative permeability

$$\mathbf{M} = \hat{\chi}_m \mathbf{H} \quad \text{where} \quad \hat{\chi}_m (= \hat{\mu}_r - 1) \text{ is the magnetic susceptibility}$$

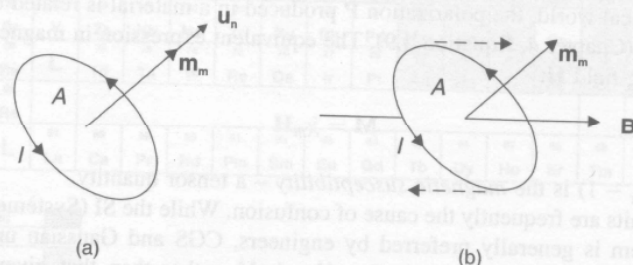


Figure 5.20 (a) Magnetic dipole moment  $\mathbf{m}_m$ . (b) In a magnetic field, a magnetic dipole moment experiences a torque.

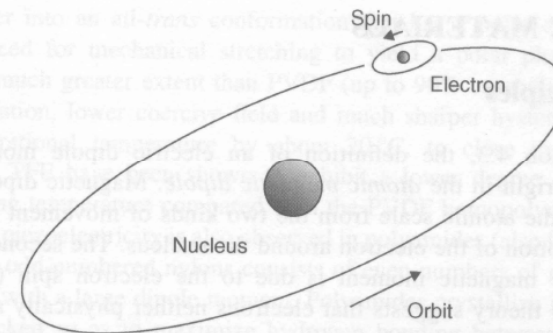
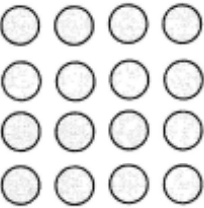
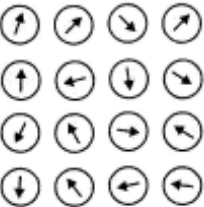
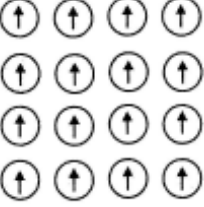


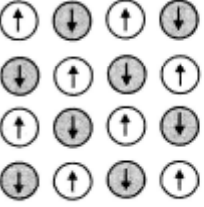
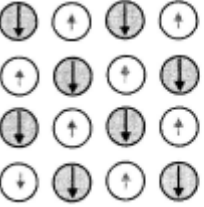
Figure 5.21 Motion of an electron around the nucleus of an atom.

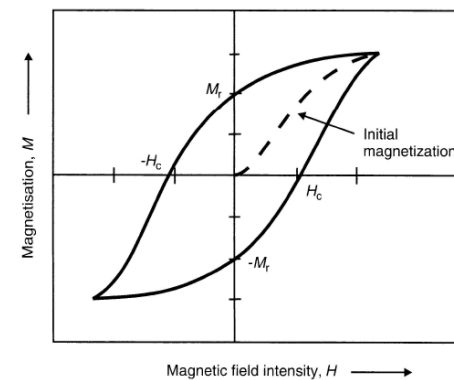
Type of magnetism	Susceptibility	Atomic arrangement	Example
Diamagnetism	Small and negative	 <p>Atoms have no magnetic moment</p>	Au, Ag, Cu, many polymers. Atoms have closed shells
Paramagnetism	Small and positive	 <p>Atoms have randomly oriented magnetic moments</p>	Gaseous and liquid oxygen. Alkali and transition metals
Ferromagnetism	Large and positive	 <p>Atoms have parallel aligned magnetic moments</p>	Fe, Co, Ni

*negative  $\chi_m$*   
 \*1) universal property  
 \*2)  $\chi_m = -1$  for the superconductor below  $T_c$

*positive  $\chi_m$*   
 Curie law  

$$\chi_m = \frac{C}{T}$$
 ( $C$  is Curie T)

Antiferromagnetism	Small and positive	 <p>Opposite and equal magnetic moments on two different sublattices</p>	Salts and oxides of transition metals. e.g. MnO, NiO
Ferrimagnetism	Large and positive	 <p>Magnetic moments on different sublattices do not cancel</p>	Ferrites

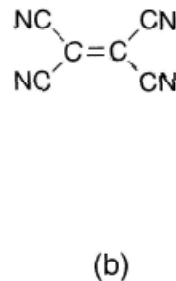
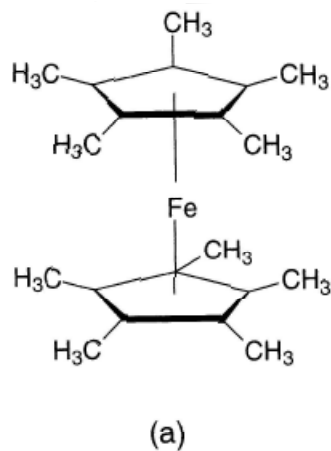


**Figure 5.25** Typical magnetization versus magnetic field intensity curve for a ferromagnetic material.  $H_c$  = coercive field;  $M_r$  = remanent magnetization.

# Organic Magnets: Molecule-based Magnets

- Molecule based magnets currently remain laboratory curiosities with no real world applications. As indicated, this is largely due to the very low [critical temperature](#) at which these materials become magnetic.
- Specific materials include purely organic magnets made of organic radicals [\[2\]](#), mixed coordination compounds with bridging organic radicals [\[3\]](#), [Prussian Blue](#) related compounds [\[4\]](#), and [charge transfer complexes](#) [\[5\]](#).
- Molecule based magnets derive their net moment from the cooperative effect of the spin-bearing molecular entities, and can display bulk [ferromagnetic](#) and [ferrimagnetic](#) behavior with a true [critical temperature](#).

W



CT complex  
Radical cation/radical anion  
T<sub>c</sub> ~4.8 K

Figure 5.26 (a) Decamethylferrocene; (b) tetracyanoethylene.