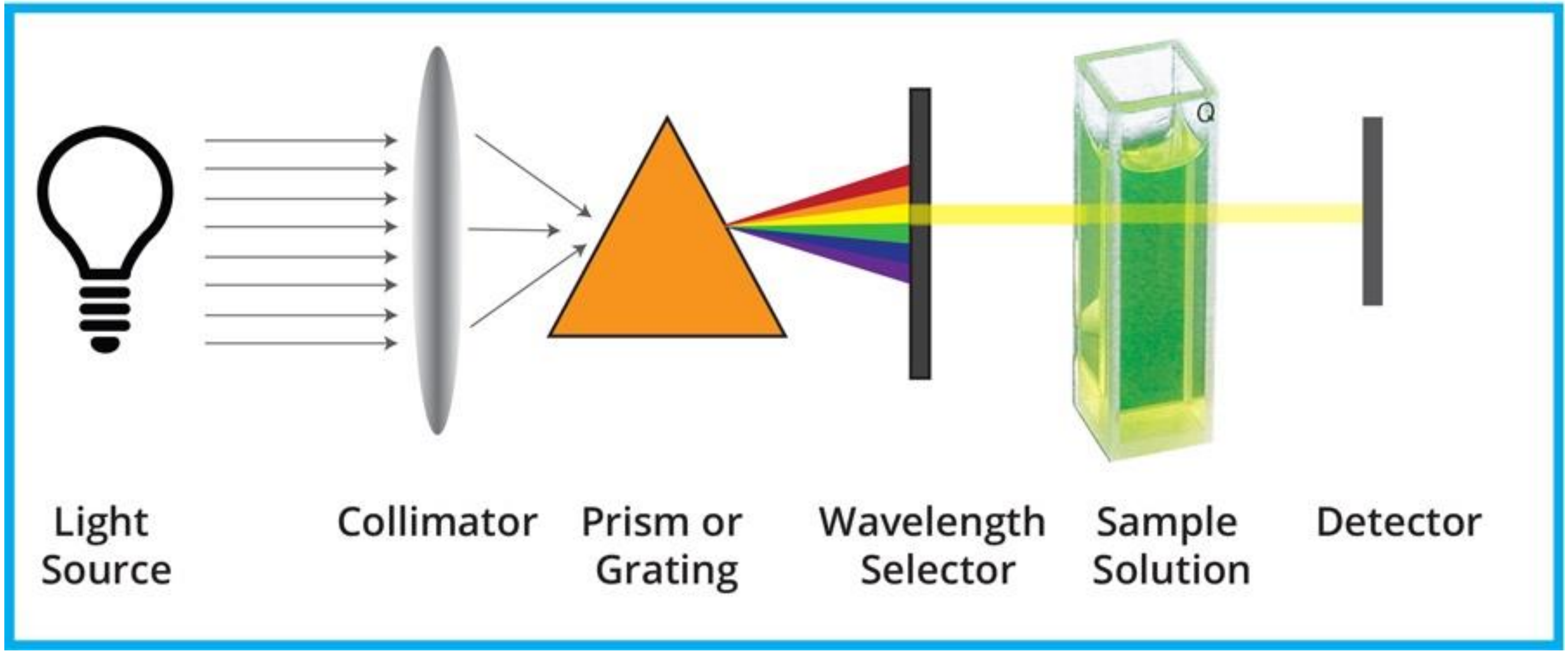
Electronic and magnetic properties of transition metal complexes



Overview

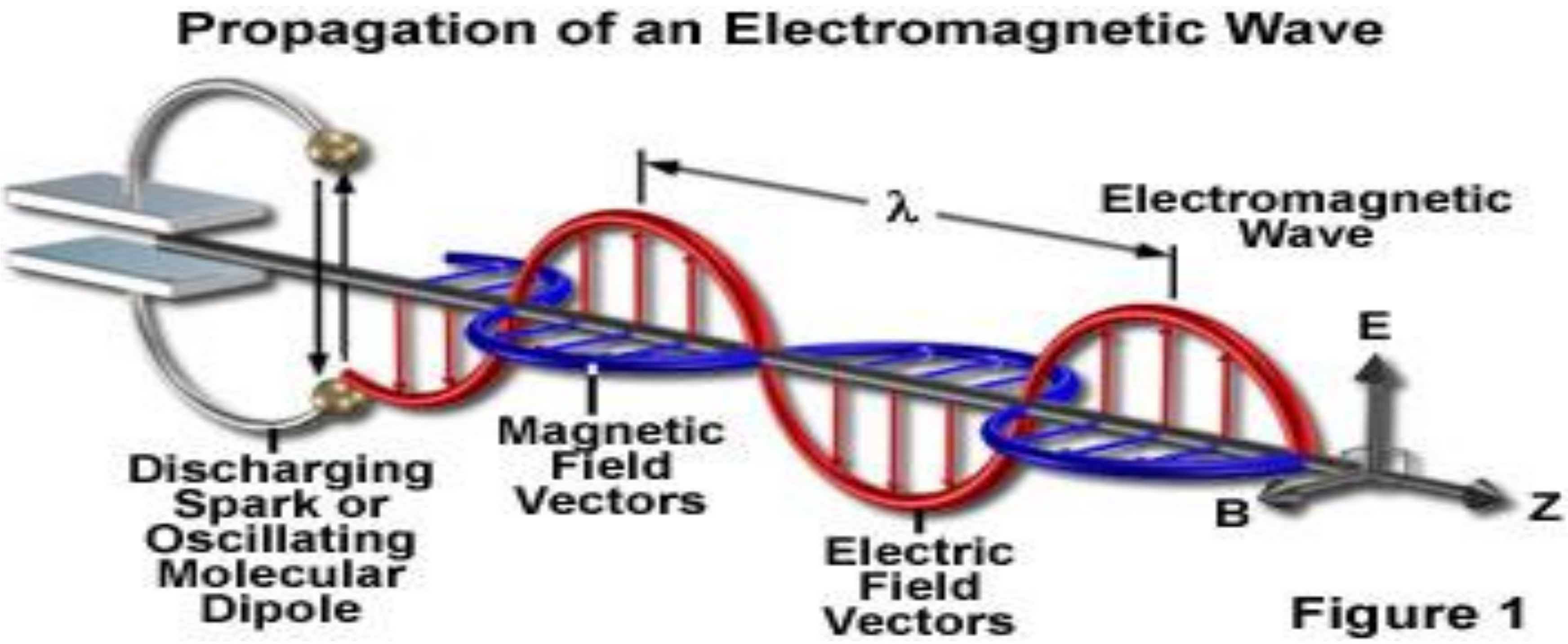
1. **Introduction**
2. **Instrumentation**
3. **How does the instrument work?**

Part (1)

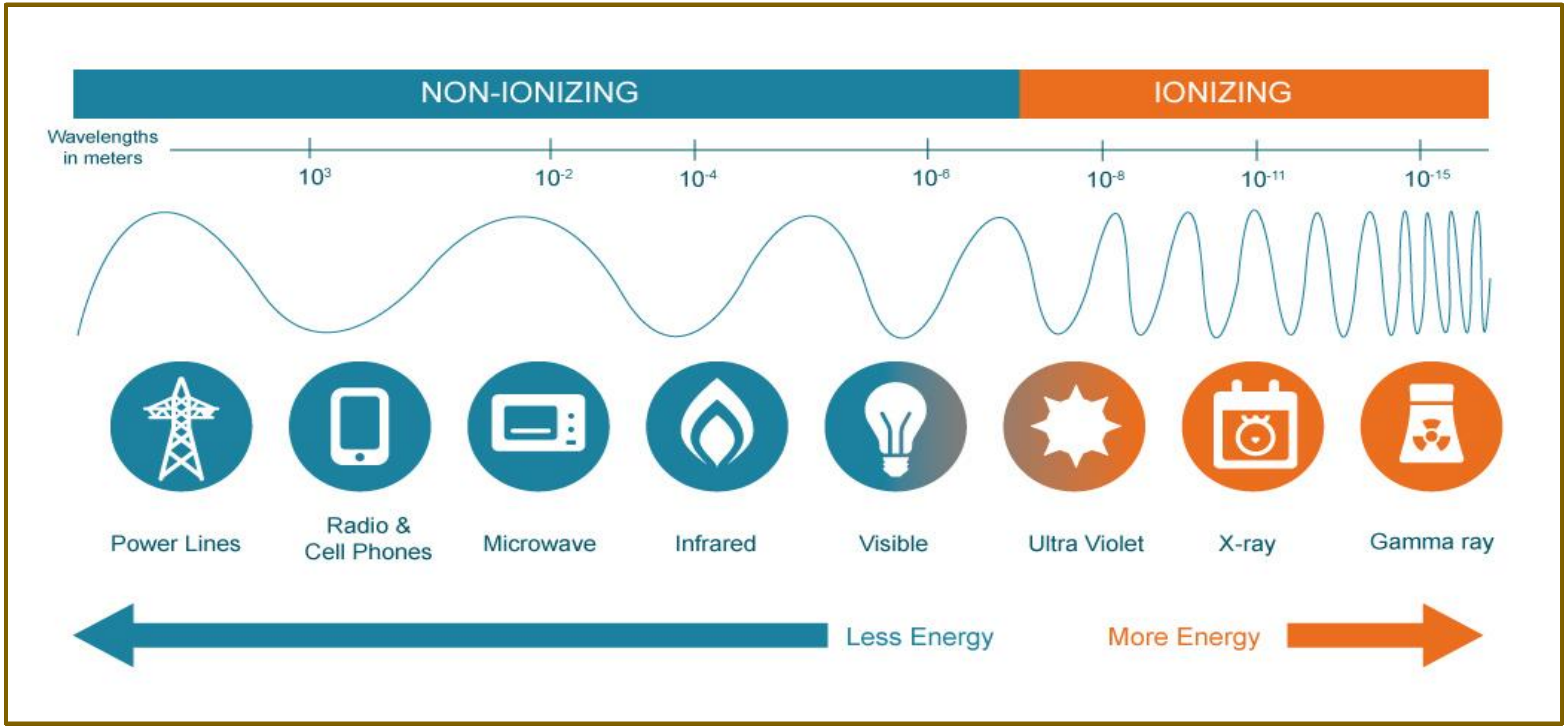
Electronic spectra of transition metal complexes

Electromagnetic radiation

- Moving charges/particles through space
- Oscillating wave like property of electric and magnetic field
- Electric and magnetic field oscillate perpendicular to each other and perpendicular to direction of wave propagation.



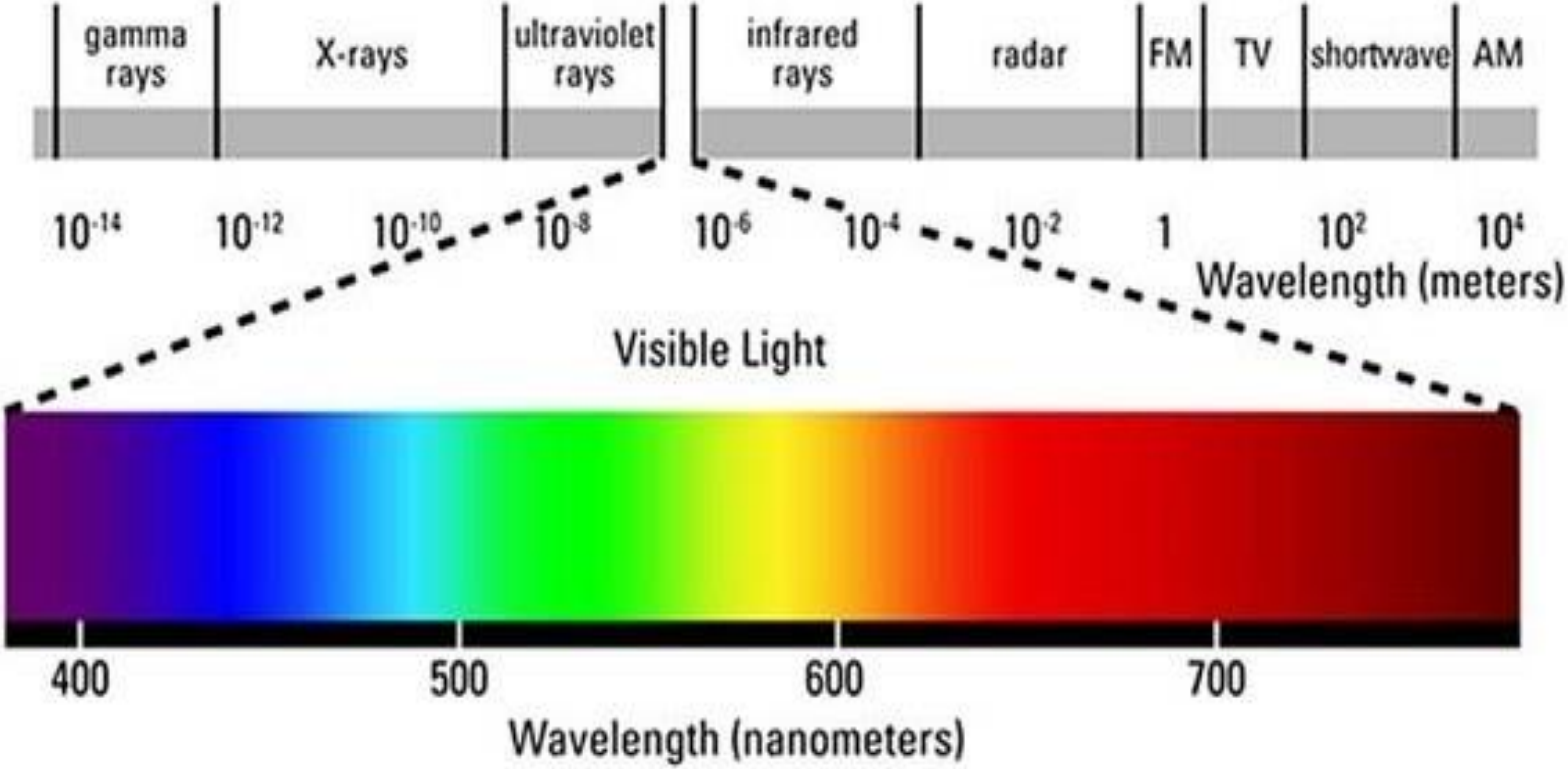
Electromagnetic spectrum ranges from Radiowaves to Gamma waves.
- Form of energy



Longer Wavelength, λ Lower Frequency, f
Lower Energy, E

Shorter Wavelength, λ
Higher Frequency, f
Higher Energy, E

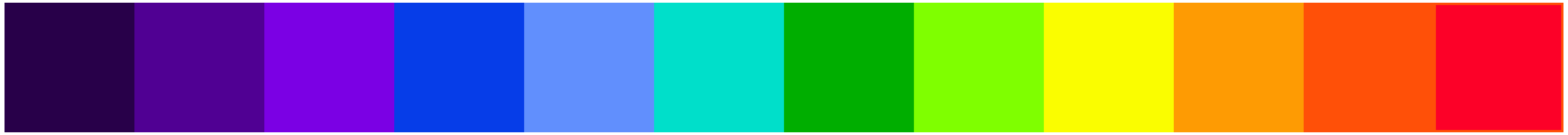
The Electromagnetic Spectrum



Electronic spectroscopy

wavelength, nm

(Each wavelength corresponds to a different color)

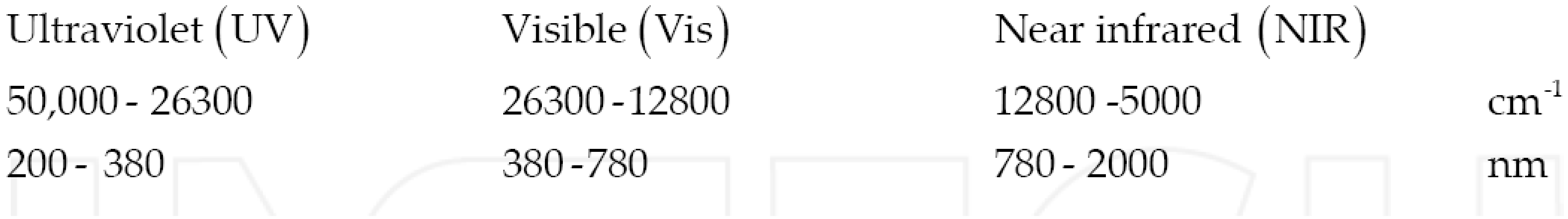


400 nm

800 nm

← higher energy

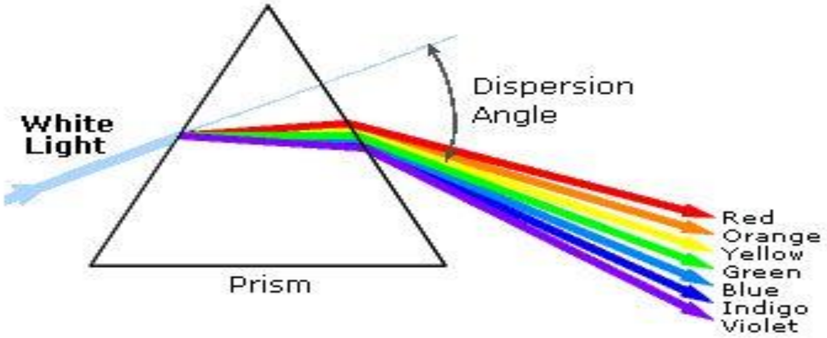
lower energy →

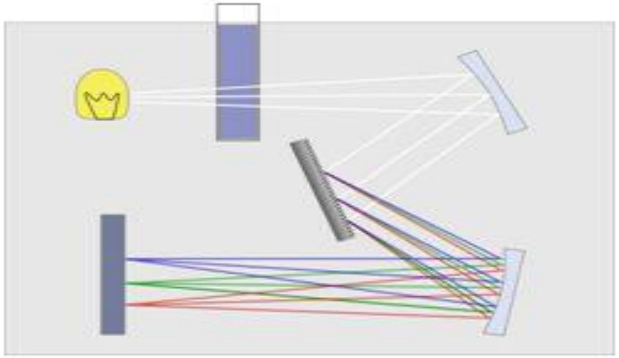


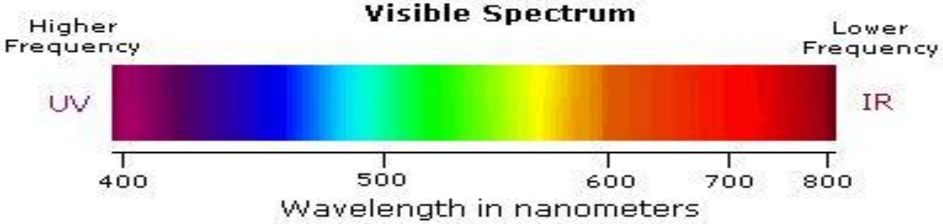
Ultraviolet (UV)	Visible (Vis)	Near infrared (NIR)	
50,000 - 26300	26300 - 12800	12800 -5000	cm^{-1}
200 - 380	380 - 780	780 - 2000	nm

UV-Vis spectroscopy

Electronic absorption spectroscopy



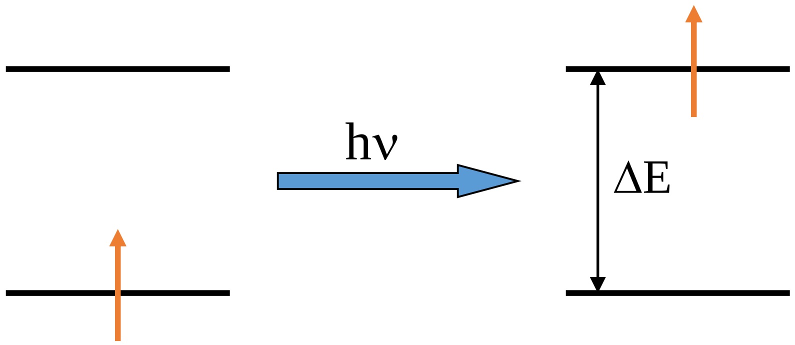


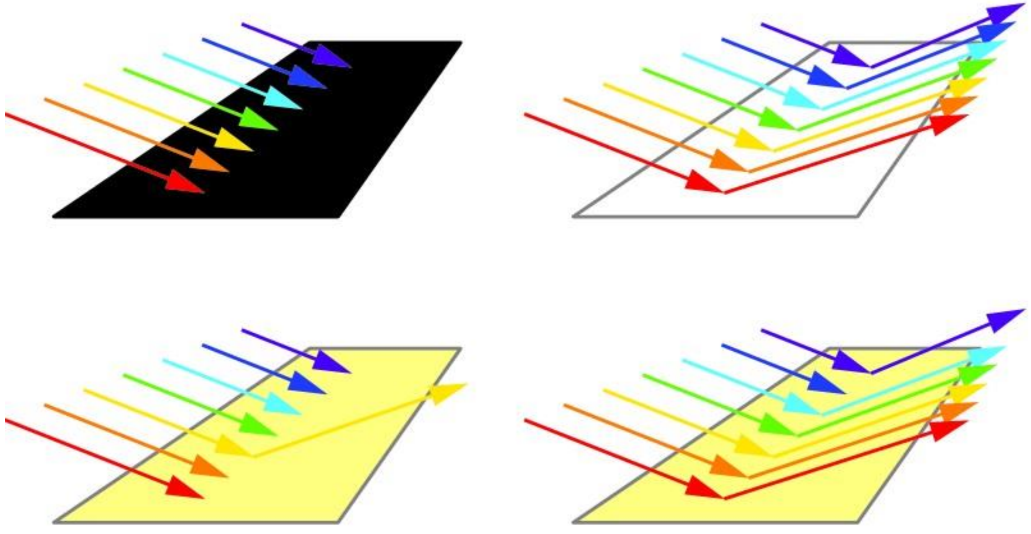


- **Violet:** 400 - 420 nm
- **Indigo:** 420 - 440 nm
- **Blue:** 440 - 490 nm
- **Green:** 490 - 570 nm
- **Yellow:** 570 - 585 nm
- **Orange:** 585 - 620 nm
- **Red:** 620 - 780 nm

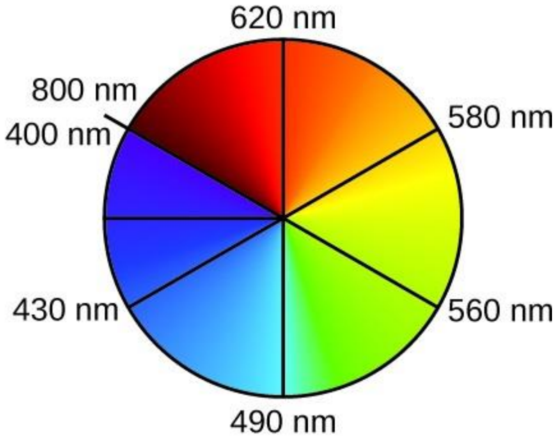
Electronic Spectroscopy

- A phenomenon of interaction of molecules with ultraviolet and visible lights.
- Absorption of photon results in electronic transition of a molecule, and electrons are promoted from ground state to higher electronic states.

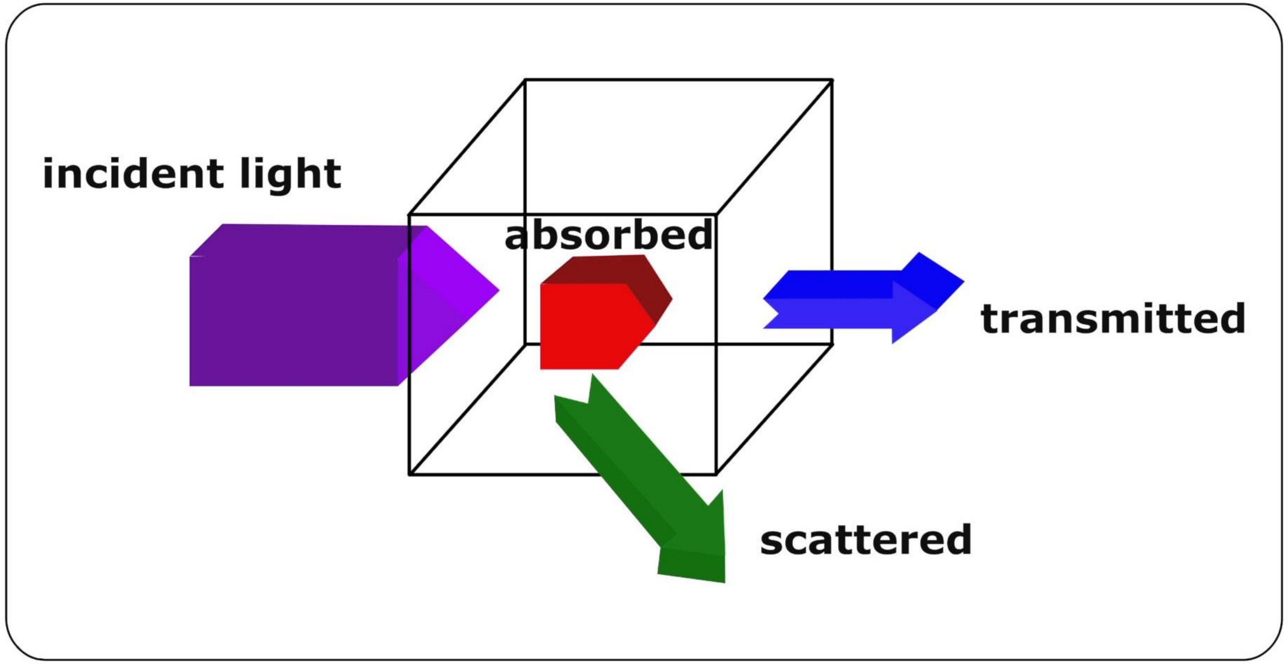


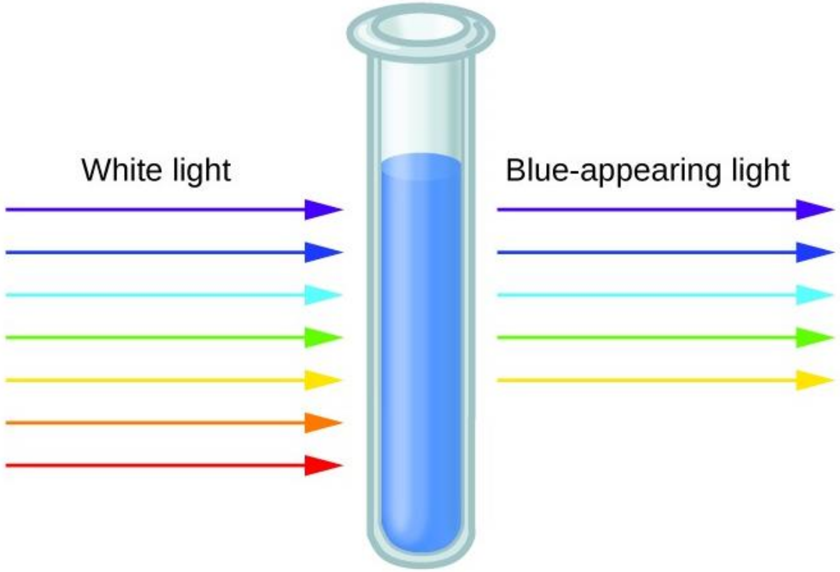


(a)


620 nm
800 nm
400 nm
580 nm
430 nm
560 nm
490 nm

(b)


incident light
absorbed
transmitted
scattered


White light
Blue-appearing light

(c)

Electromagnetic radiation

- **Travel at speed of light, $c = \lambda\nu \rightarrow 3.0 \times 10^8$ m/s**
- **Light Particle – photon have energy given by -> $E = h\nu$**
- **Energy photon - proportional to frequency**

$$C = \lambda\nu$$

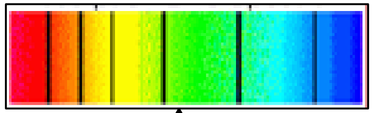
C = velocity (m/s)
λ = wavelength (m)
ν = Frequency (Hz)

$$E = h\nu$$

E = Energy (J)
h = blank's constant = 6.626×10^{-34} Js
ν = Frequency (Hz)

$$E = \frac{hc}{\lambda}$$

Electronic Spectroscopy



↑

Electrons in excited state

↑

Radiation absorbed

↑

Absorb radiation to excited state

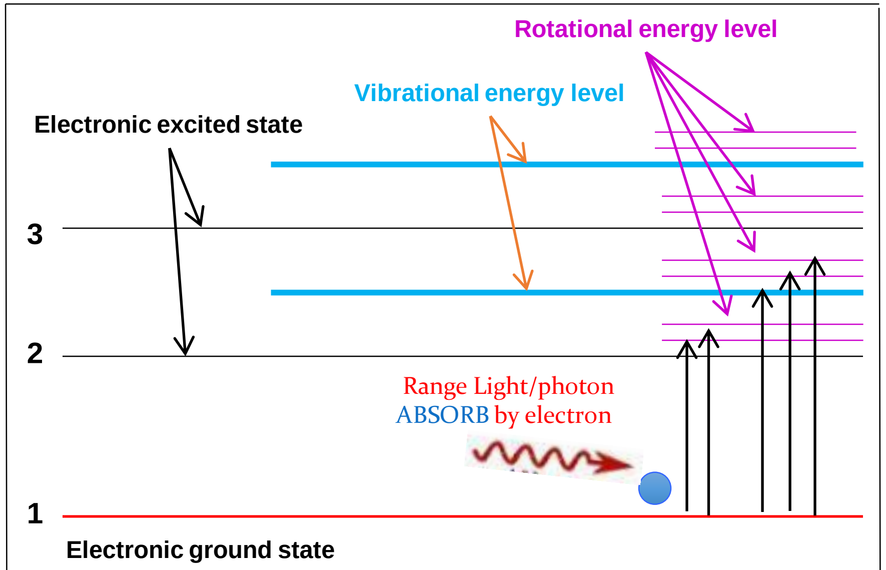
↑

Electrons from ground state

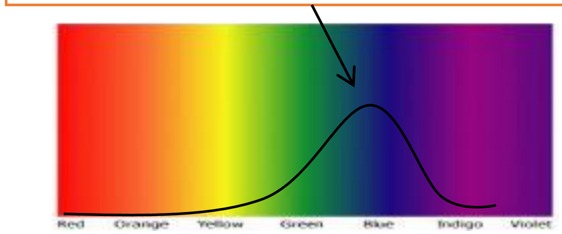
Absorption spectrum is broad/continuous
Ions in solution (Solvent)

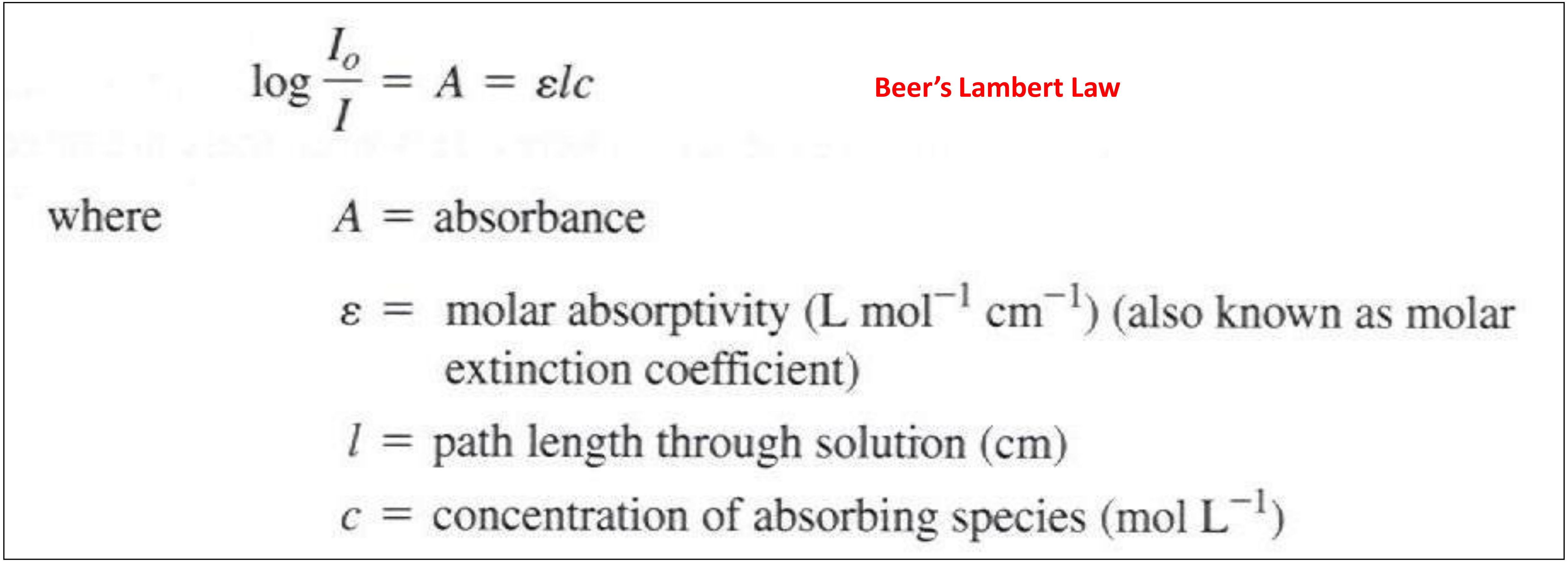
↓

Absorption spectrum for ions in solution
↓
Surrounded by ligand and solvent
↓
Have electronic excitation transition state + vibrational/rotational energy level
↓
Continuous broad spectrum



Whole range of wavelength/broad spectrum can be absorbed to excite electron to electronic/vibrational/ rotational level





$$\log \frac{I_o}{I} = A = \varepsilon l c$$

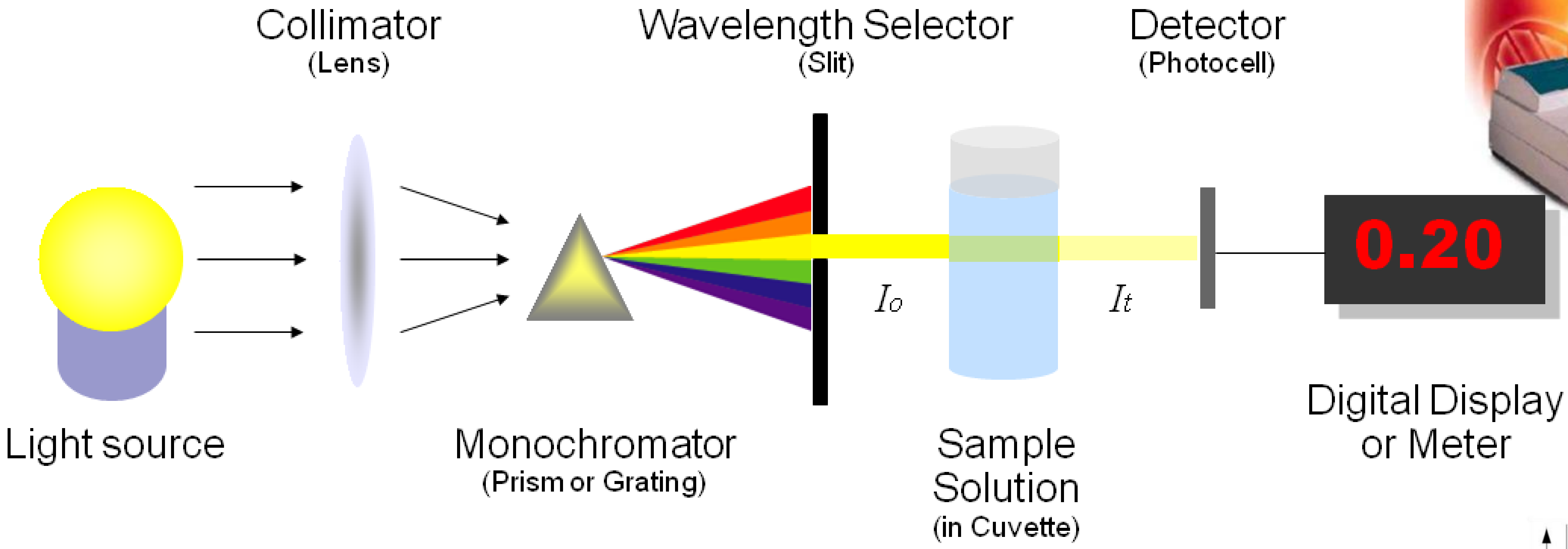
Beer’s Lambert Law

where A = absorbance

ε = molar absorptivity ($\mathrm{L\ mol^{-1}\ cm^{-1}}$) (also known as molar extinction coefficient)

l = path length through solution (cm)

c = concentration of absorbing species ($\mathrm{mol\ L^{-1}}$)



Collimator
(Lens)

Wavelength Selector
(Slit)

Detector
(Photocell)

Light source

Monochromator
(Prism or Grating)

I_o

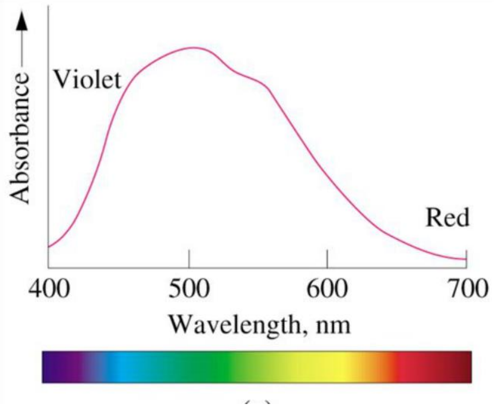
Sample
Solution
(in Cuvette)

I_t

0.20

Digital Display
or Meter

UV-Visible spectrophotometer



ELECTRONIC SPECTROSCOPY

- This is also known as UV-vis spectroscopy and covers the region from 200 to 800 nm of the electromagnetic spectrum.
- The region from 200 to 400 nm is called the ultraviolet (UV) and that from 400 to 800 nm is known as the visible region.
- A substance appeared colored when the emitted light falls in this visible region.
- This spectroscopy is used to find out the geometry of complexes because the number of bands seen in the visible region due to d-d transitions depends on the geometry of the complex.

Part (II)

Instrumentation

How does the instrument work?

Applications

Types of Instruments

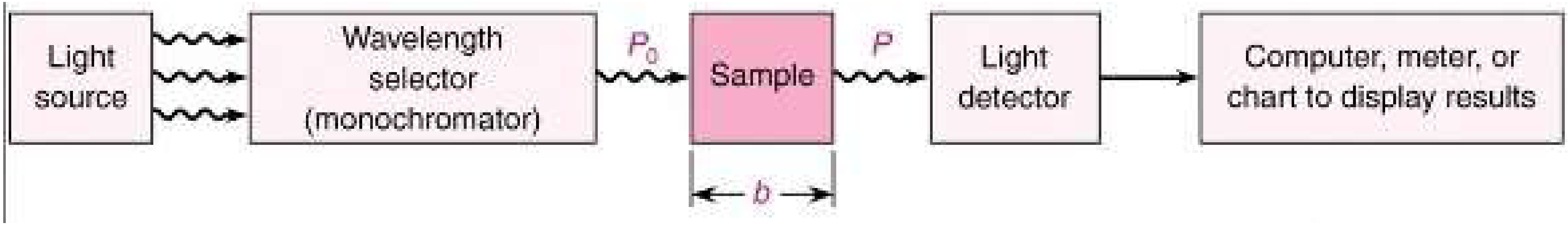
Single beam spectrophotometers

and

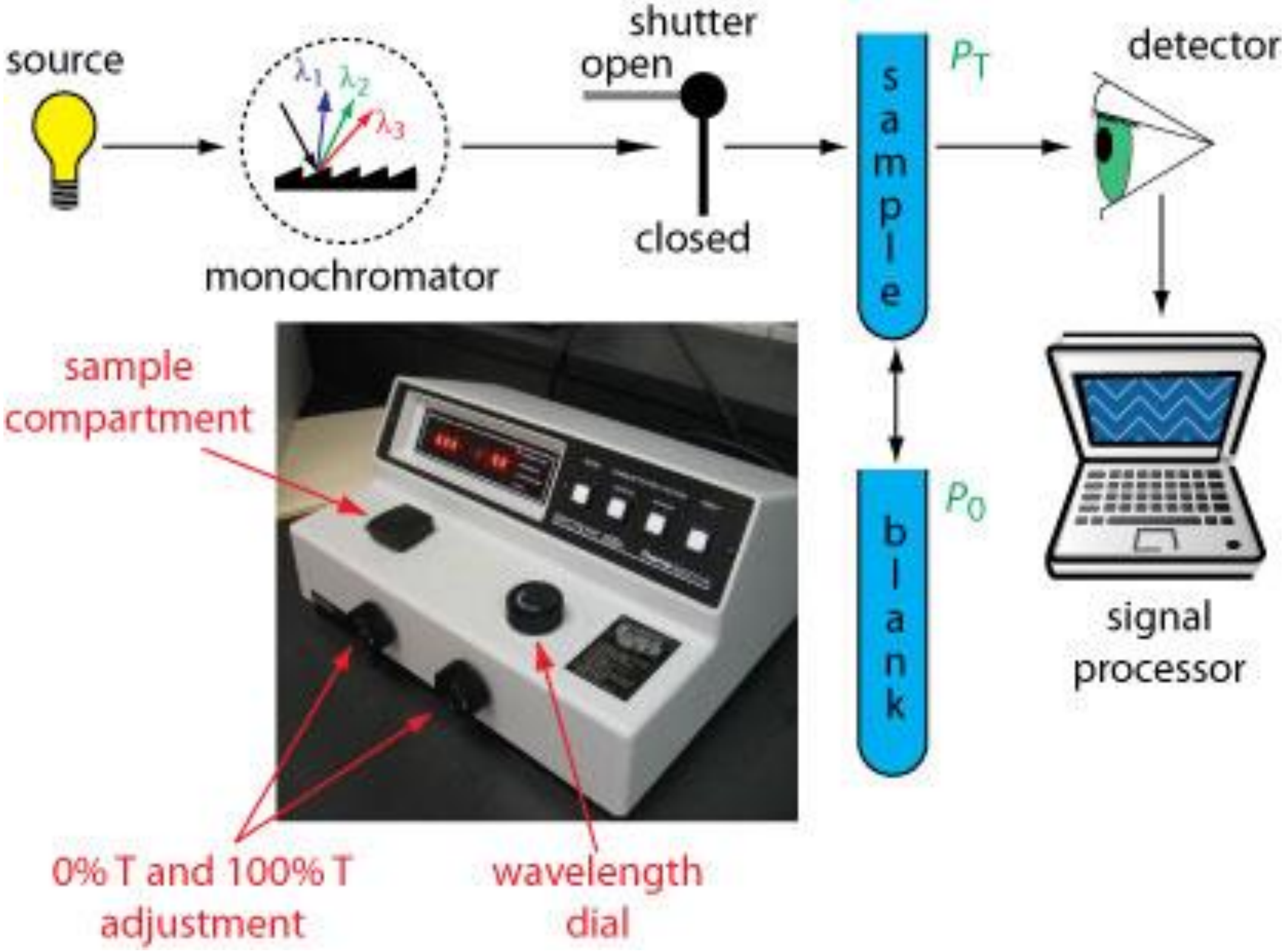
Double beam spectrophotometer

Single beam spectrophotometers

To measure the intensity of the incident light the sample must be removed so that the reference can be placed each time. This type of spectrometer is usually less expensive and less complicated.



Single beam spectrophotometers

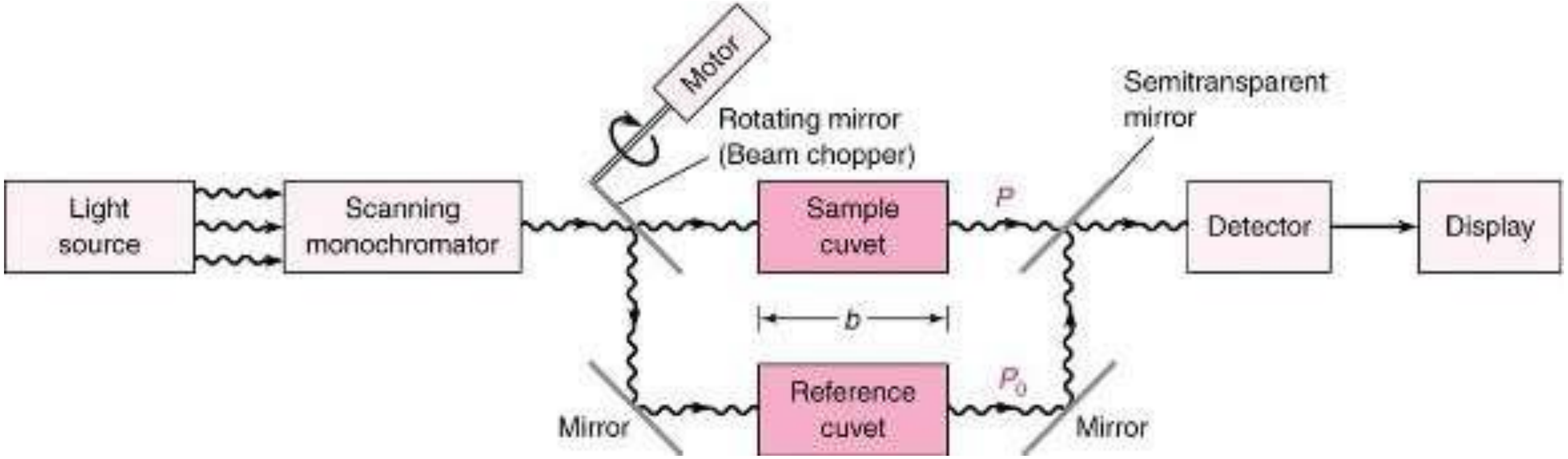


How does it work?

https://www.youtube.com/watch?v=xHQM4BbR040

Double beam spectrometer:

- In this type, before it reaches the sample, the light source is split into two separate beams. From these one passes through the sample and second one is used for reference. This gives an advantage because the reference reading and sample reading can take place at the same time



Double beam spectrometer:

How does it work?

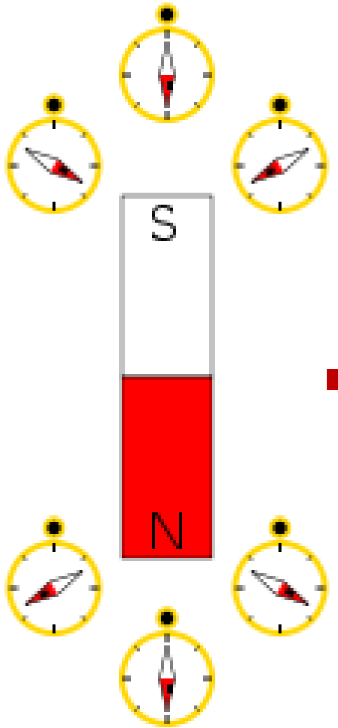
https://www.youtube.com/watch?v=s5uIVQGFDE4

https://www.youtube.com/watch?v=TV_T_zEUPe4

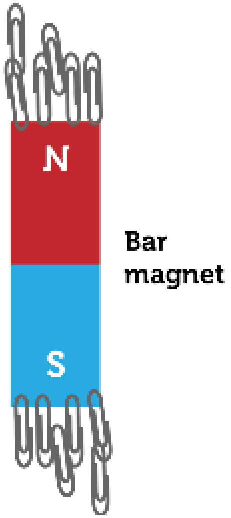
Applications

1. **Concentration measurement**
2. **Detection of impurities**
3. **Chemical kinetics**
4. **Detection of functional group**
5. **Molecular weight determination**

https://www.youtube.com/watch?v=nVkS8oimyHg



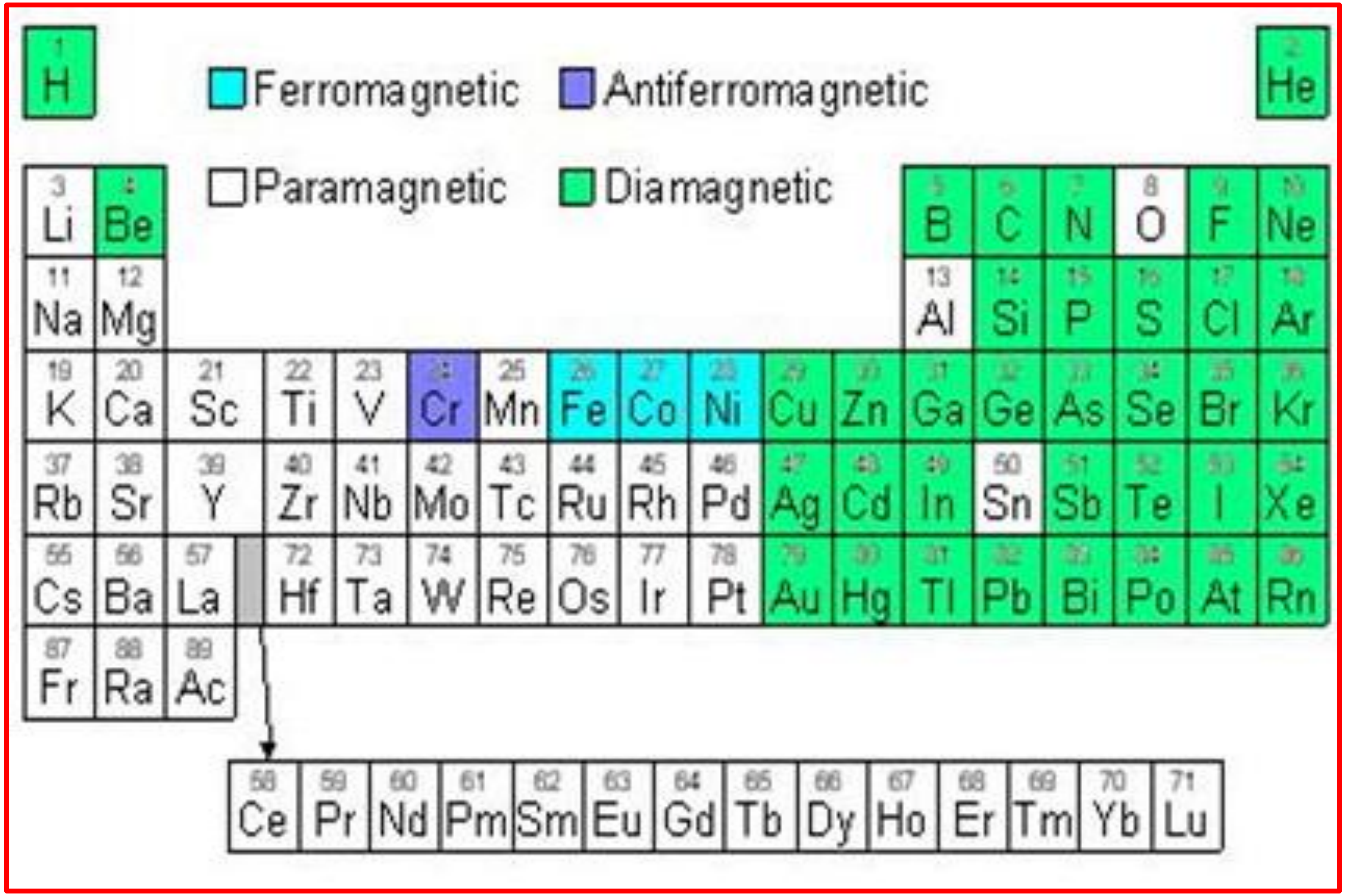
Magnetic properties of Transition metal complexes



Magnetic studies

- One of the most valuable fields of application of magneto chemistry is the investigation of transition metal complexes.
- Magnetic measurements indicate the electronic configuration of the d-shell of the transition metal.
- Magnetic measurements can provide information on the electronic structure and oxidation state, and in some cases on the symmetry properties of the transition metal central atom.

Elements that can be magnet



🟦 Ferromagnetic 🟪 Antiferromagnetic

☐ Paramagnetic 🟩 Diamagnetic

🟩 1 H																	🟩 2 He
☐ 3 Li	🟩 4 Be											🟩 5 B	🟩 6 C	🟩 7 N	☐ 8 O	🟩 9 F	🟩 10 Ne
☐ 11 Na	☐ 12 Mg											☐ 13 Al	🟩 14 Si	🟩 15 P	🟩 16 S	🟩 17 Cl	🟩 18 Ar
☐ 19 K	☐ 20 Ca	☐ 21 Sc	☐ 22 Ti	☐ 23 V	🟪 24 Cr	☐ 25 Mn	🟦 26 Fe	🟦 27 Co	🟦 28 Ni	🟩 29 Cu	🟩 30 Zn	🟩 31 Ga	🟩 32 Ge	🟩 33 As	🟩 34 Se	🟩 35 Br	🟩 36 Kr
☐ 37 Rb	☐ 38 Sr	☐ 39 Y	☐ 40 Zr	☐ 41 Nb	☐ 42 Mo	☐ 43 Tc	☐ 44 Ru	☐ 45 Rh	☐ 46 Pd	🟩 47 Ag	🟩 48 Cd	🟩 49 In	☐ 50 Sn	🟩 51 Sb	🟩 52 Te	🟩 53 I	🟩 54 Xe
☐ 55 Cs	☐ 56 Ba	☐ 57 La	☐ 72 Hf	☐ 73 Ta	☐ 74 W	☐ 75 Re	☐ 76 Os	☐ 77 Ir	☐ 78 Pt	🟩 79 Au	🟩 80 Hg	🟩 81 Tl	🟩 82 Pb	🟩 83 Bi	🟩 84 Po	🟩 85 At	🟩 86 Rn
☐ 87 Fr	☐ 88 Ra	☐ 89 Ac															

☐ 58 Ce	☐ 59 Pr	☐ 60 Nd	☐ 61 Pm	☐ 62 Sm	☐ 63 Eu	☐ 64 Gd	☐ 65 Tb	☐ 66 Dy	☐ 67 Ho	☐ 68 Er	☐ 69 Tm	☐ 70 Yb	☐ 71 Lu

Application of Magnets


Loud Speaker


Printer


Medical Equipment


Magnetic Levitation


Motor


Sensor


Mobile Cover

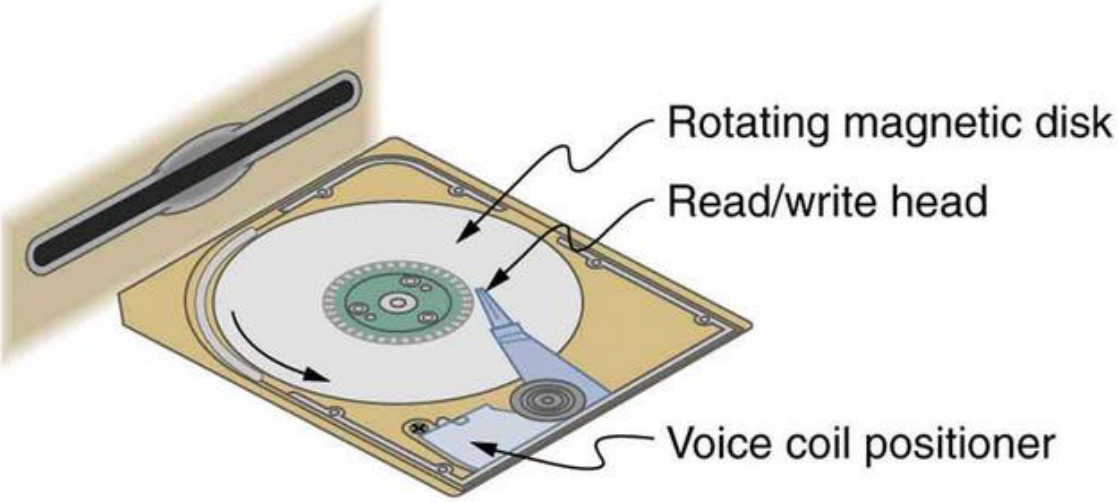

Gift Box Packing


Magnetic Toy


Car holder


Wind Turbine


VCM


Rotating magnetic disk
Read/write head
Voice coil positioner


4027 1484
EXPIRES END
03/09


MetroCard
SingleRide

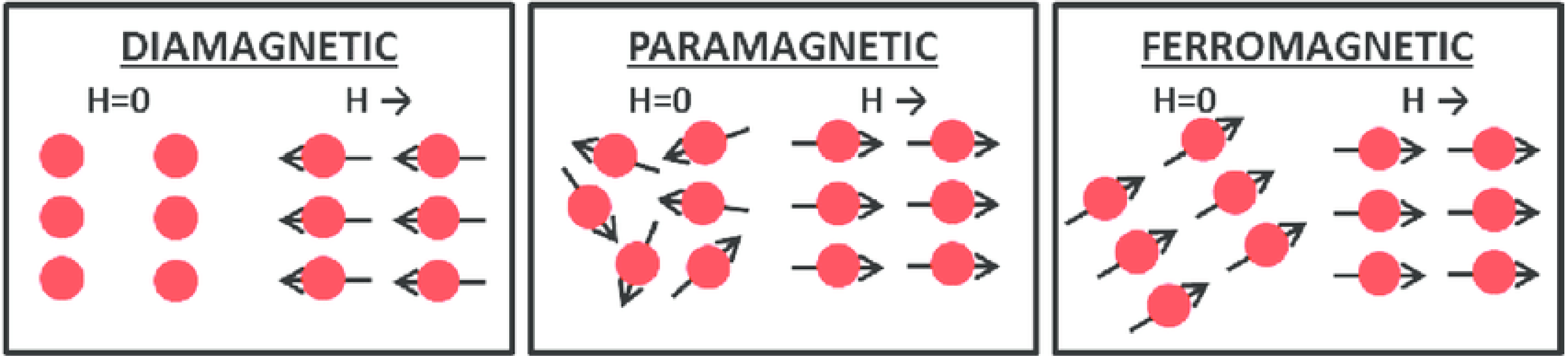

90

What is Magnetism?

- **Magnetism is a phenomenon of attracting magnetic substances like iron, nickel, cobalt, etc.**
- **Magnetism is a property of materials that respond to an applied magnetic field that cause the material to be either attracted or repelled.**
- **A body possessing the property of magnetism is called a magnet.**

Types of Magnetisms

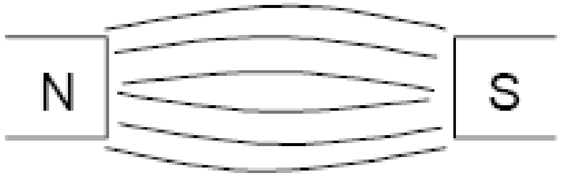
1. **Diamagnetism**
2. **Paramagnetism**
3. **Ferromagnetism**



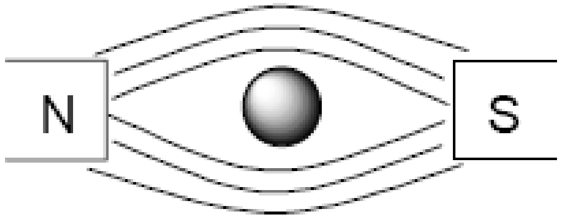
1. Diamagnetism, which is shown by every molecule. This is due to the inductive action of the external magnetic field on the electron cloud.

2. Paramagnetism, which is shown only by molecules containing unpaired electrons. It arises from the spin and orbital moments of the unpaired electrons. The external magnetic field tends to align the intrinsic magnetic moment of the molecule in the direction of the field.

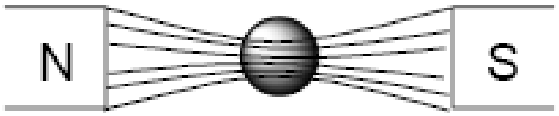
	Diamagnetic	**Paramagnetic**
Electron pairing	↑↓ ↑↓ ↑↓ No unpaired electrons	↑↓ ↑↓ ↑ At least one unpaired electron



vacuum



diagmagnetic



paramagnetic

Where does the magnetic moment come from?

Each electron has a magnetic moment

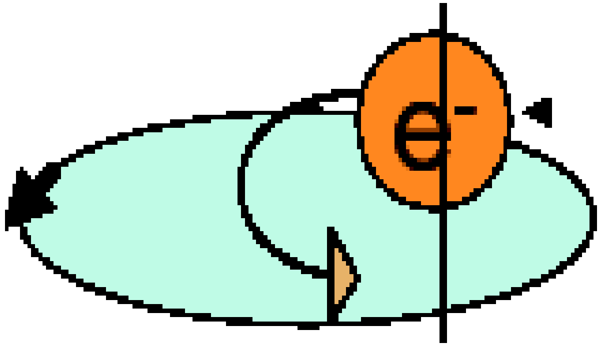
spin angular momentum

orbital angular momentum

Spin motion of e about its own Axis also generates a magnetic field

Orbital motion of e generates current and magnetic field

$$\mu_{total} = \mu_{orbital} + \mu_{spin}$$



MAGNETIC SUSCEPTIBILITY

- Magnetic susceptibility is the measure of the magnetic properties of a material in the field of electromagnetism.
- If the magnetic susceptibility is positive in nature, then the material is paramagnetic, or ferromagnetic, or anti-ferromagnetic in nature. In this reference, the presence of the material results in the strengthening of the magnetic field. Magnetic susceptibility is high in value when it comes to Ferro magnets.
- If the magnetic susceptibility is negative in nature, then the material is diamagnetic in nature. This results in weakening of the magnetic field in presence of the material.

Magnetic susceptibility

- Susceptibility (χ) = internal magnetization
  - Diamagnetic ($\chi < 0$) opposes applied field
  - Paramagnetic ($\chi > 0$) reinforces applied field
  - Superparamagnetic and ferromagnetic ($\chi >> 0$)
- Most biological tissues are weakly diamagnetic

Determination of Susceptibility

Gouy method

- Magnetic susceptibility is related to the force experienced by a substance in a magnetic field.
- Magnetic susceptibility is measured by Gouy's balance by using Cobalt mercury tetrathiocyanate as a calibrant ($Hg[Co(SCN)_4]$ ($\chi_g = 16.44 \times 10^{-6}$ CGS units at 20°C).
- Diamagnetic correction was made using Pascal's constant.

Why are we doing this experiment?

- Magnetic Properties reveal numbers of unpaired electrons.
- The number of unpaired electrons tell us about oxidation state, geometry, ligand field strength, etc…

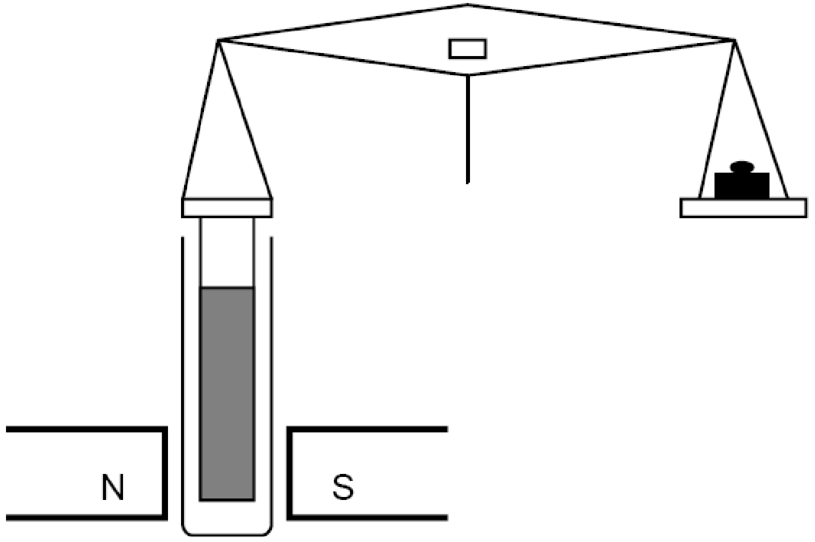


FIGURE 3 : THE TRADITIONAL GOUY BALANCE

How are we doing this experiment?

- We are using a Johnson-Matthey MSB-Auto Magnetic Susceptibility Balance
- It uses the Evan’s detector which is a modified Gouy Method

Paramagnetism and diamagnetism

Gouy Balance

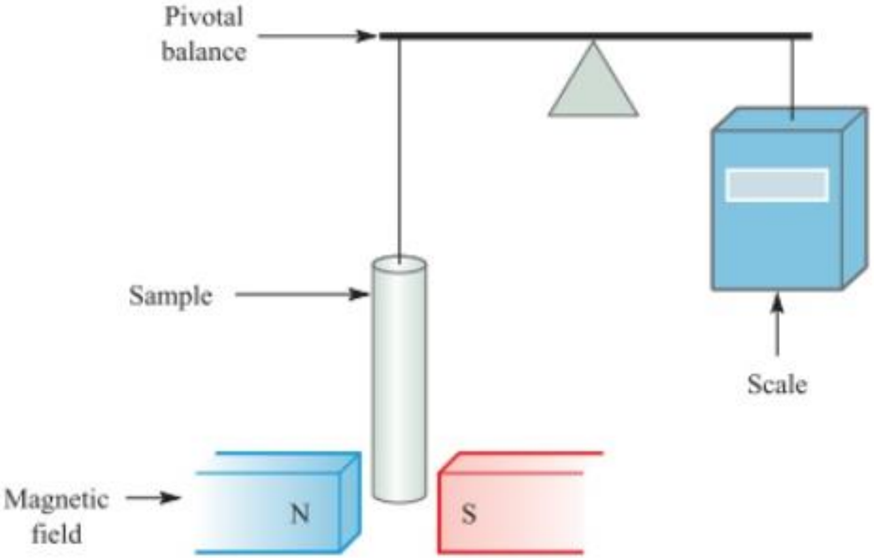
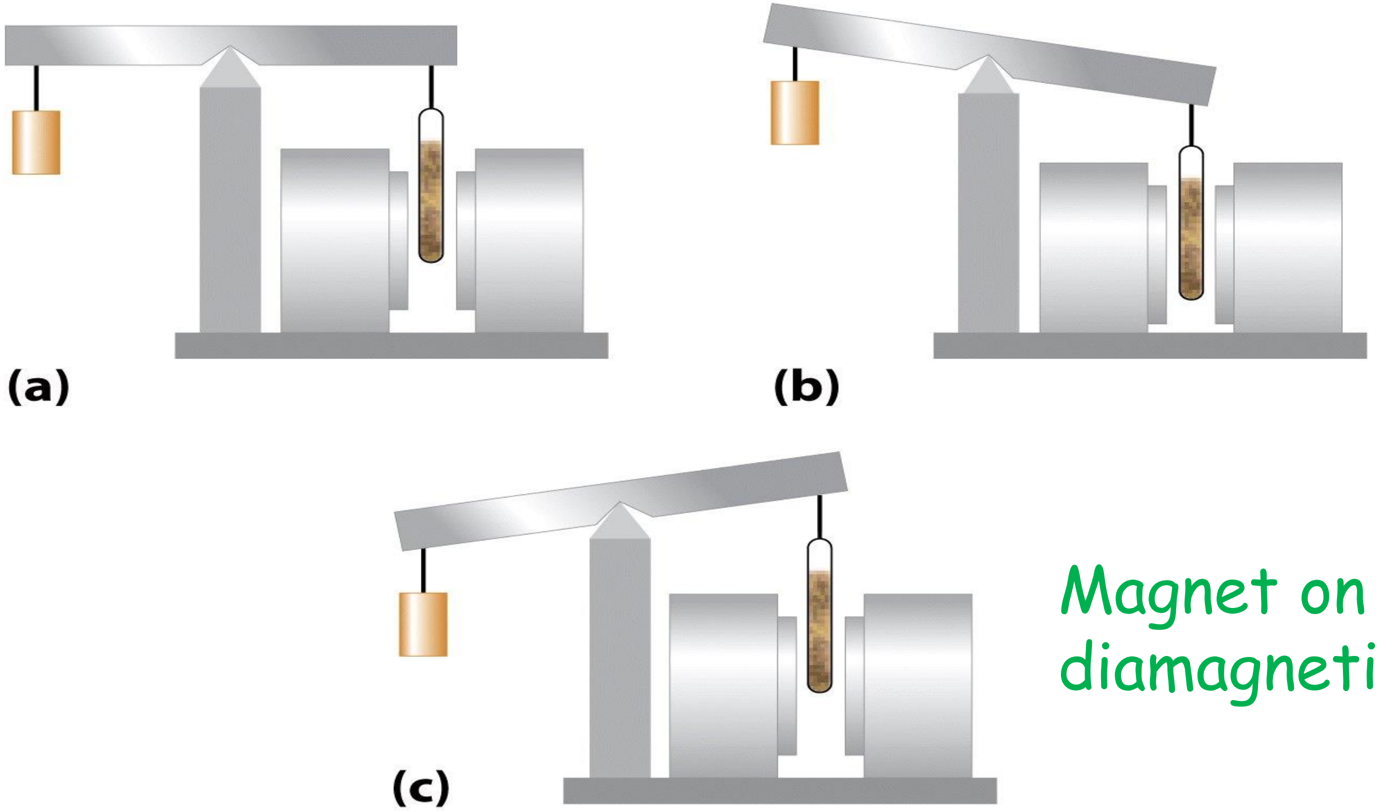


Fig. 20.21 Schematic representation of a Gouy balance.

Magnet off

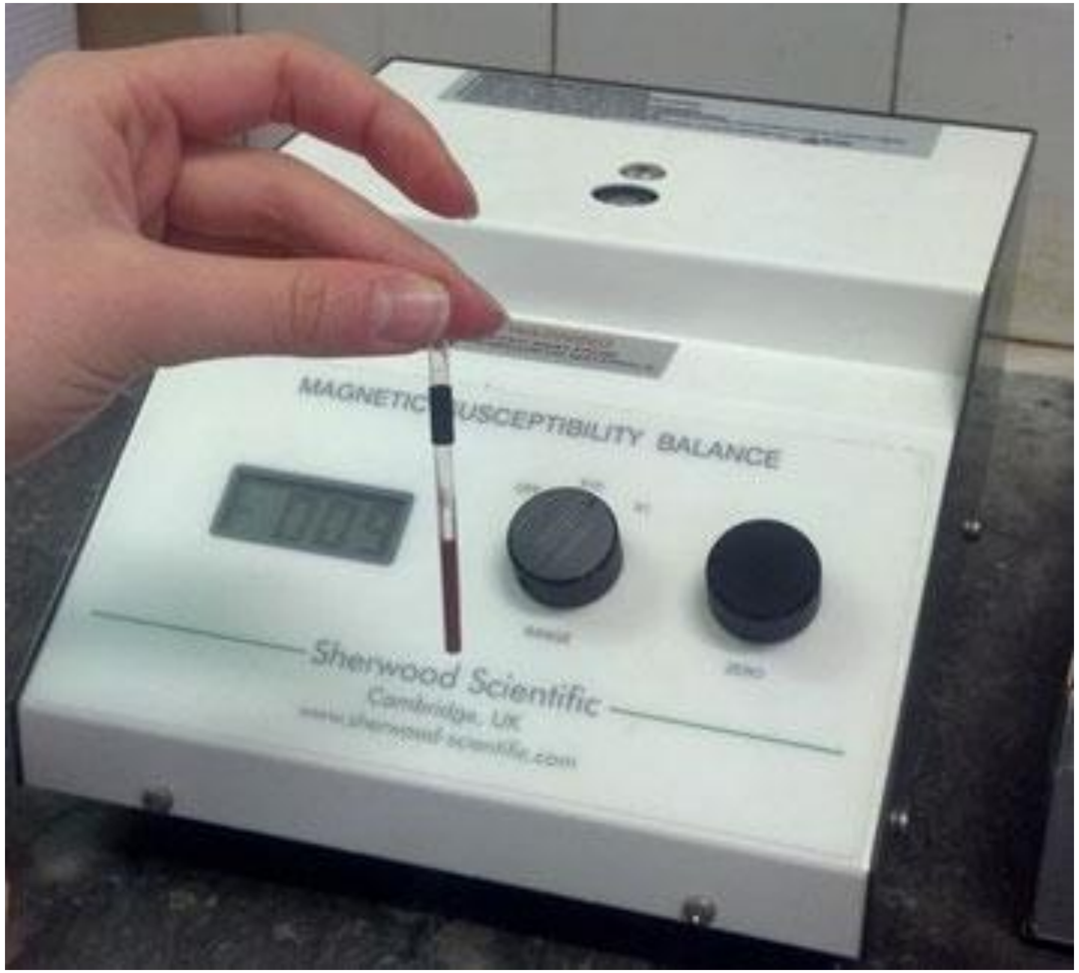
Magnet on
Paramagnetic

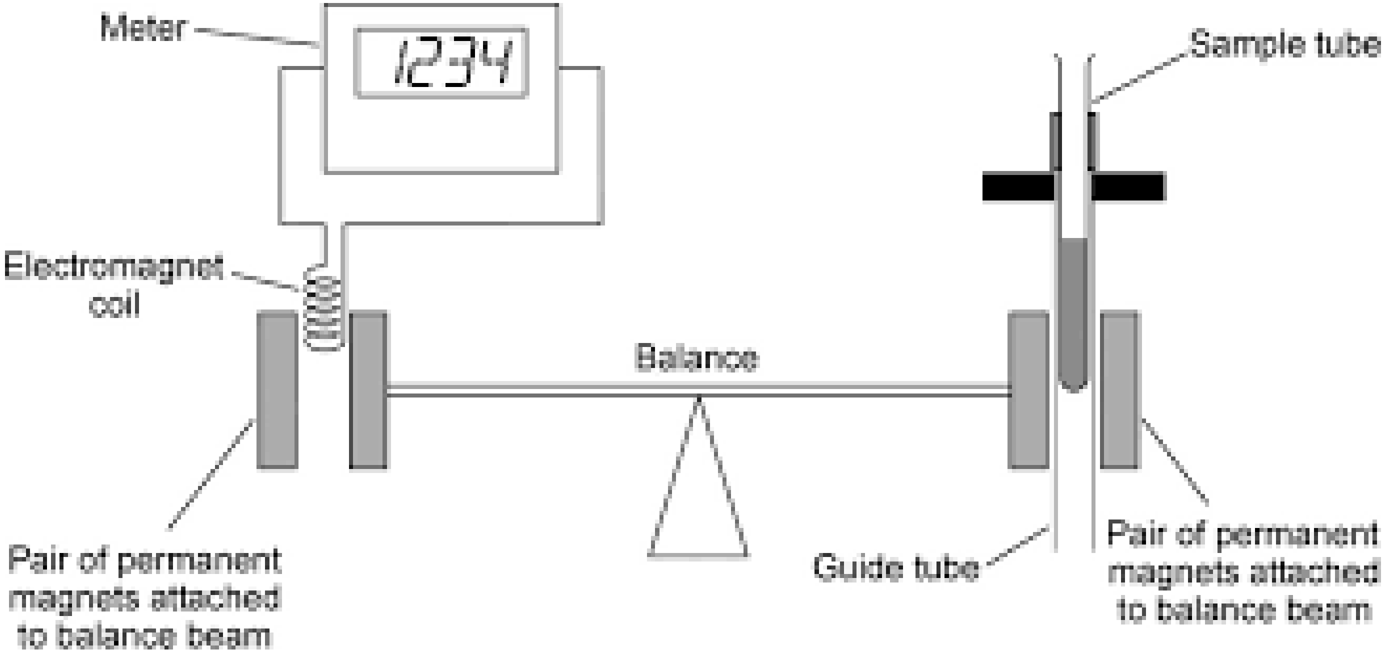


Magnet on
diamagnetic

Magnetic Properties:

An **Evans balance**, also known as a **Johnson-Matthey balance**





Johnson-Matthey balance

- The Johnson-Matthey magnetic susceptibility balance is very similar to the traditional Gouy balance but, instead of measuring the force that a magnet exerts on a sample, the opposite force that the sample exerts on a suspended permanent magnet is observed.
- **The mass susceptibility, χ_g , is calculated using**

$$\chi_g = \frac{C_{bal}\, l(R - R_o)}{10^9\, m}$$

where:

l = sample length (cm)

m= sample mass (g)

R= reading for tube plus sample

R_o = empty tube reading

C_{bal} = balance calibration constant

- **The molar susceptibility, χ_m, is then calculated by multiplying χ_g by the molecular mass of the substance.**

$$\chi_m = (\chi_g)(\text{Mol. Wt})$$

χ_m = + ve value → paramagnetic and,
χ_m = – ve value → diamagnetic.

- **The molar susceptibility measured is a sum of the paramagnetic contribution from the unpaired electrons in the metal ion and the diamagnetic contributions from the ligands and the counter ions. This can be expressed by:**

$$\chi_{\text{total}} = \chi_{\text{para}} + \chi_{\text{dia.}} \text{ (L+ ions)}$$

Therefore

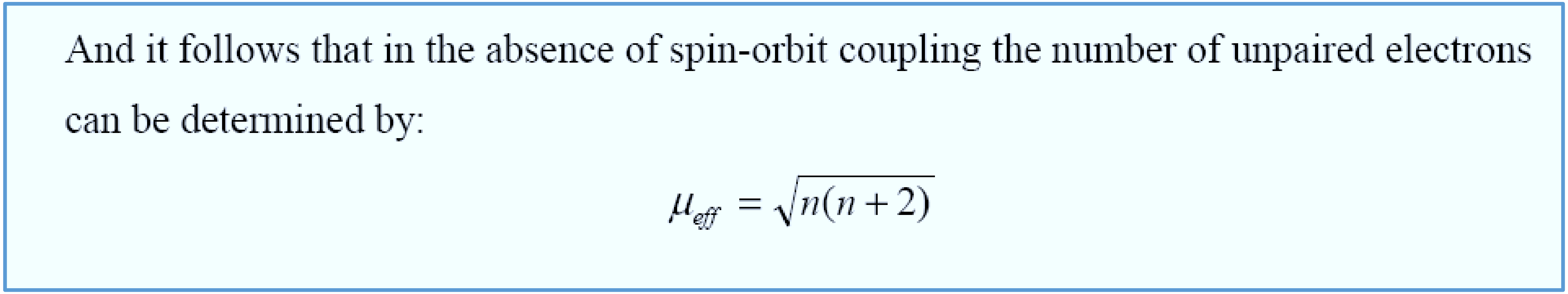
$$\chi_{\text{para}} = \chi_{\text{corr.}} = \chi_{\text{total}} - \chi_{\text{dia.}}$$

Note: $\chi_{\text{dia.}}$ is negative

- **The diamagnetism factors for common ligands and ions as well as the Pascal constants used to calculate the diamagnetic corrections for complex ligands.**

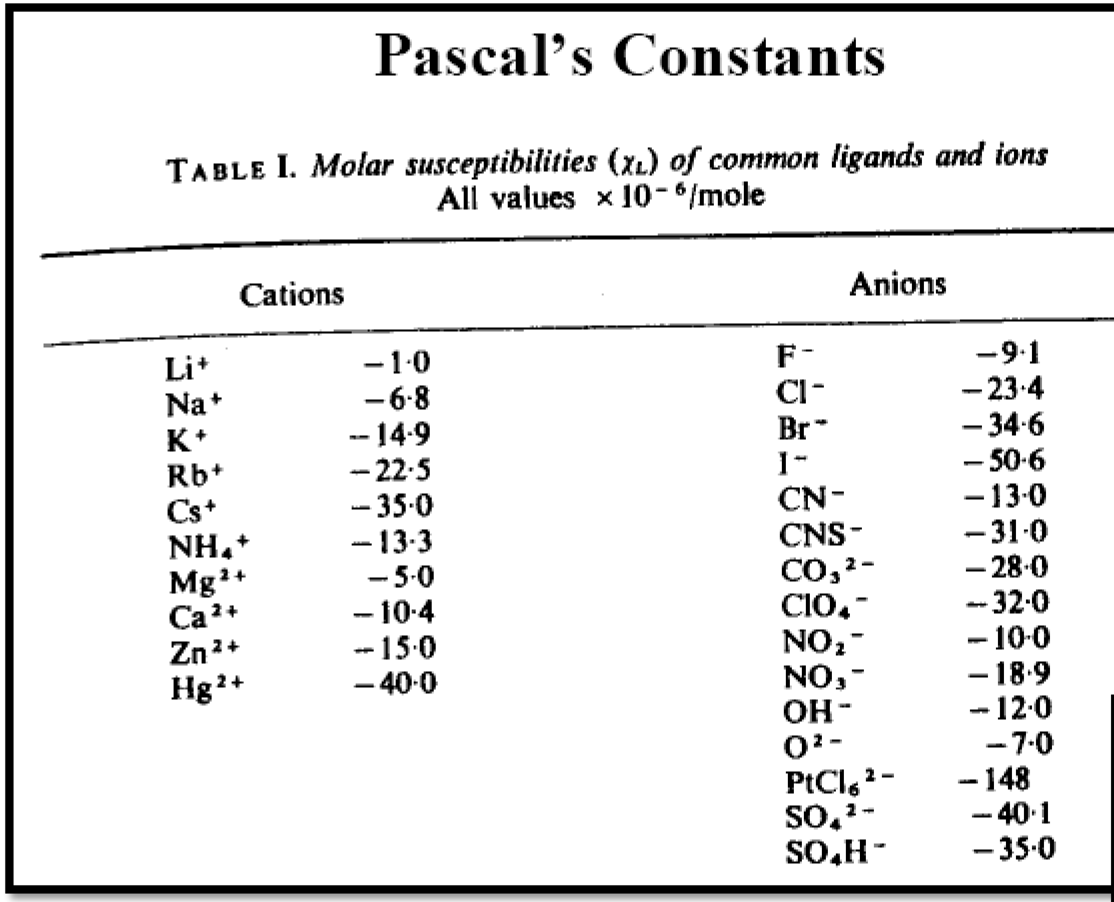
- Once the $\chi_{corr.}$ Is determined μ_{eff} can be calculated using:

$$\mu_{eff} = 2.84 \times \sqrt{\chi_M . \ T}$$



And it follows that in the absence of spin-orbit coupling the number of unpaired electrons can be determined by:

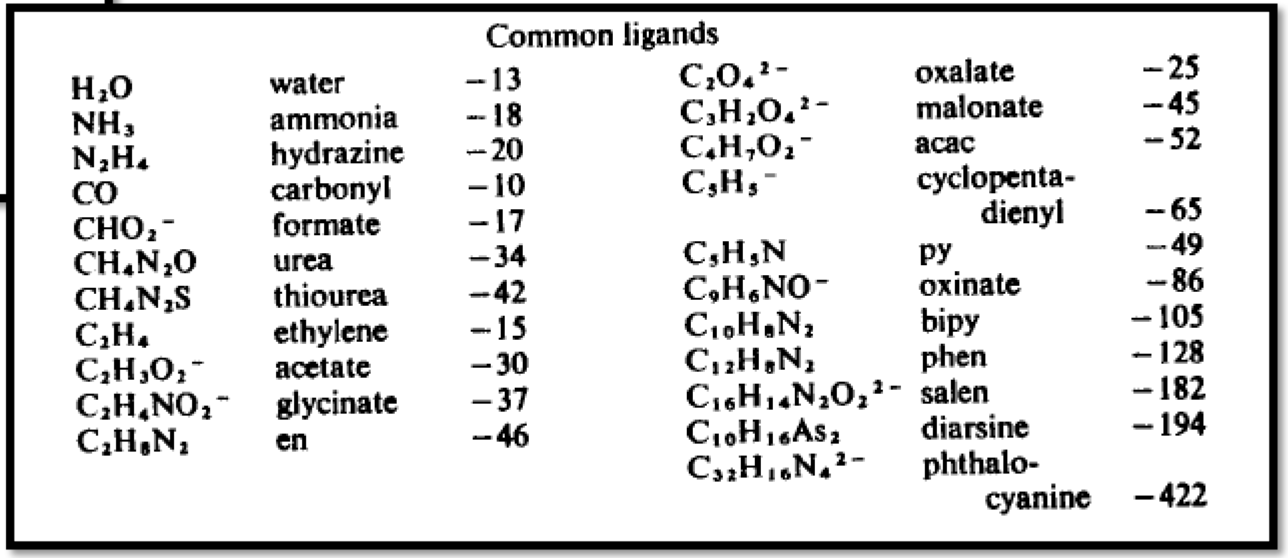
$$\mu_{eff} = \sqrt{n(n+2)}$$



Pascal's Constants

TABLE I. *Molar susceptibilities* (χ_L) *of common ligands and ions*
All values $\times 10^{-6}$/mole

Cations		Anions	
Li^+	−1·0	F^-	−9·1
Na^+	−6·8	Cl^-	−23·4
K^+	−14·9	Br^-	−34·6
Rb^+	−22·5	I^-	−50·6
Cs^+	−35·0	CN^-	−13·0
NH_4^+	−13·3	CNS^-	−31·0
Mg^{2+}	−5·0	CO_3^{2-}	−28·0
Ca^{2+}	−10·4	ClO_4^-	−32·0
Zn^{2+}	−15·0	NO_2^-	−10·0
Hg^{2+}	−40·0	NO_3^-	−18·9
		OH^-	−12·0
		O^{2-}	−7·0
		$PtCl_6^{2-}$	−148
		SO_4^{2-}	−40·1
		SO_4H^-	−35·0



Common ligands

H_2O	water	−13	$C_2O_4^{2-}$	oxalate	−25
NH_3	ammonia	−18	$C_3H_2O_4^{2-}$	malonate	−45
N_2H_4	hydrazine	−20	$C_4H_7O_2^-$	acac	−52
CO	carbonyl	−10	$C_5H_5^-$	cyclopentadienyl	−65
CHO_2^-	formate	−17	C_5H_5N	py	−49
CH_4N_2O	urea	−34	$C_9H_6NO^-$	oxinate	−86
CH_4N_2S	thiourea	−42	$C_{10}H_8N_2$	bipy	−105
C_2H_4	ethylene	−15	$C_{12}H_8N_2$	phen	−128
$C_2H_3O_2^-$	acetate	−30	$C_{16}H_{14}N_2O_2^{2-}$	salen	−182
$C_2H_4NO_2^-$	glycinate	−37	$C_{10}H_{16}As_2$	diarsine	−194
$C_2H_8N_2$	en	−46	$C_{32}H_{16}N_4^{2-}$	phthalocyanine	−422

Use the table in your notebook for diamagnetic corrections

$MC_{13}H_{28}N_4Cl_2PF_6$

$(6)(13)+(28)(2.93)+(4)(4.61)+(2)(23.4)+(26.3)+(6)(9.1) = -319 \text{ x } 10^{-6}$ cm^3/mol

Calculate the corrected χ_M

$\chi_M = \chi_g - \chi_{dia}$ (diamag. Correc)

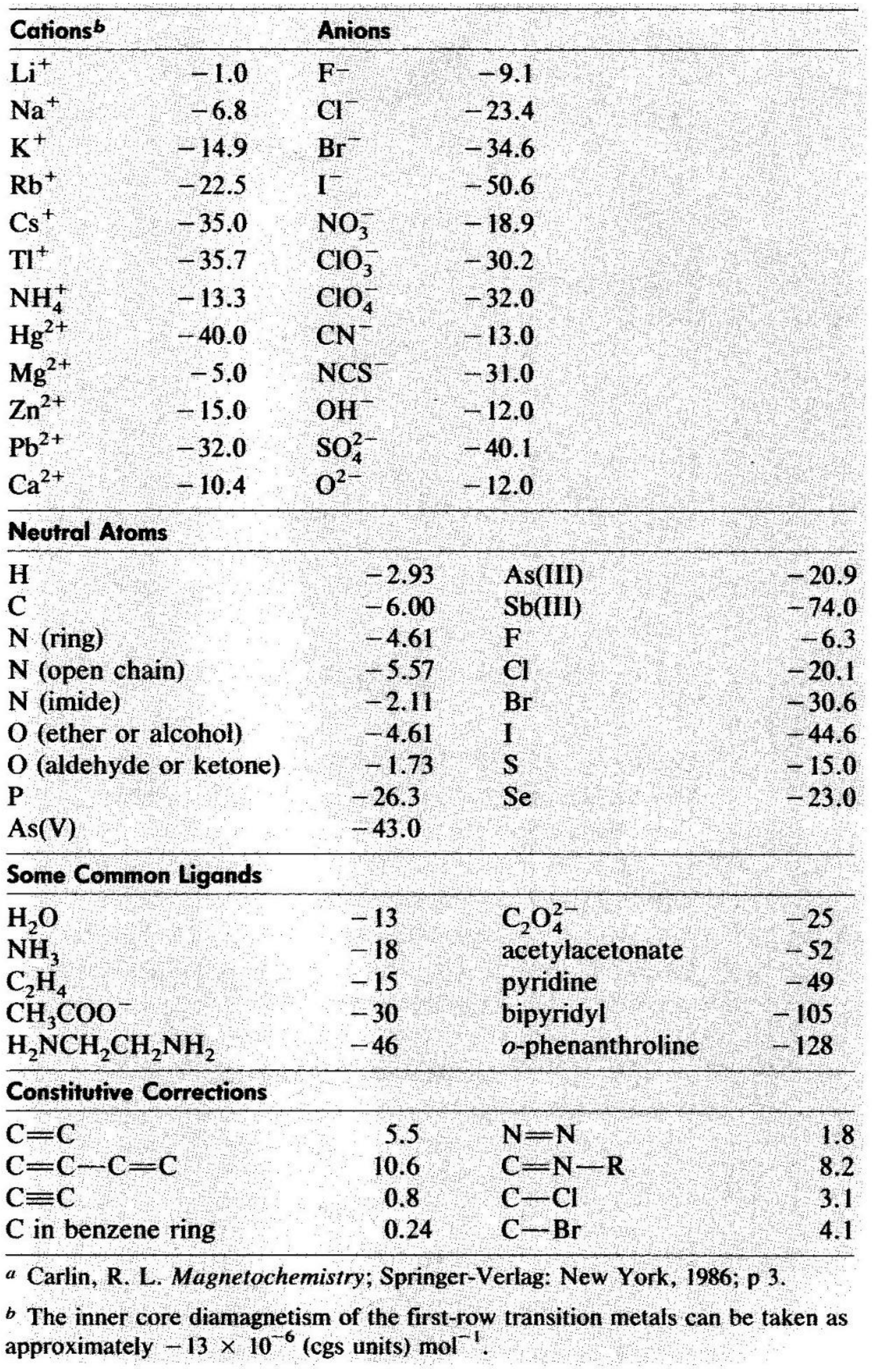
$\chi_M = (3.11 \text{ x } 10^{-3} \text{ cm}^3/\text{mol}) – (-319 \text{ x } 10^{-6} \text{ cm}^3/\text{mol}) = 3.43 \text{ x } 10^{-3}$ cm^3/mol

Calculate the magnetic moment = μ_{eff}

$\mu_{eff} = 2.84[(\chi_M)(T)]^{½}$

$\mu_{eff} = 2.84[(3.43 \text{ x } 10^{-3} \text{cm}^3/\text{mol})(298\text{K})]^{½}$

μ_{eff} = 2.86 J/T = 2.86 Bohr Magnetons



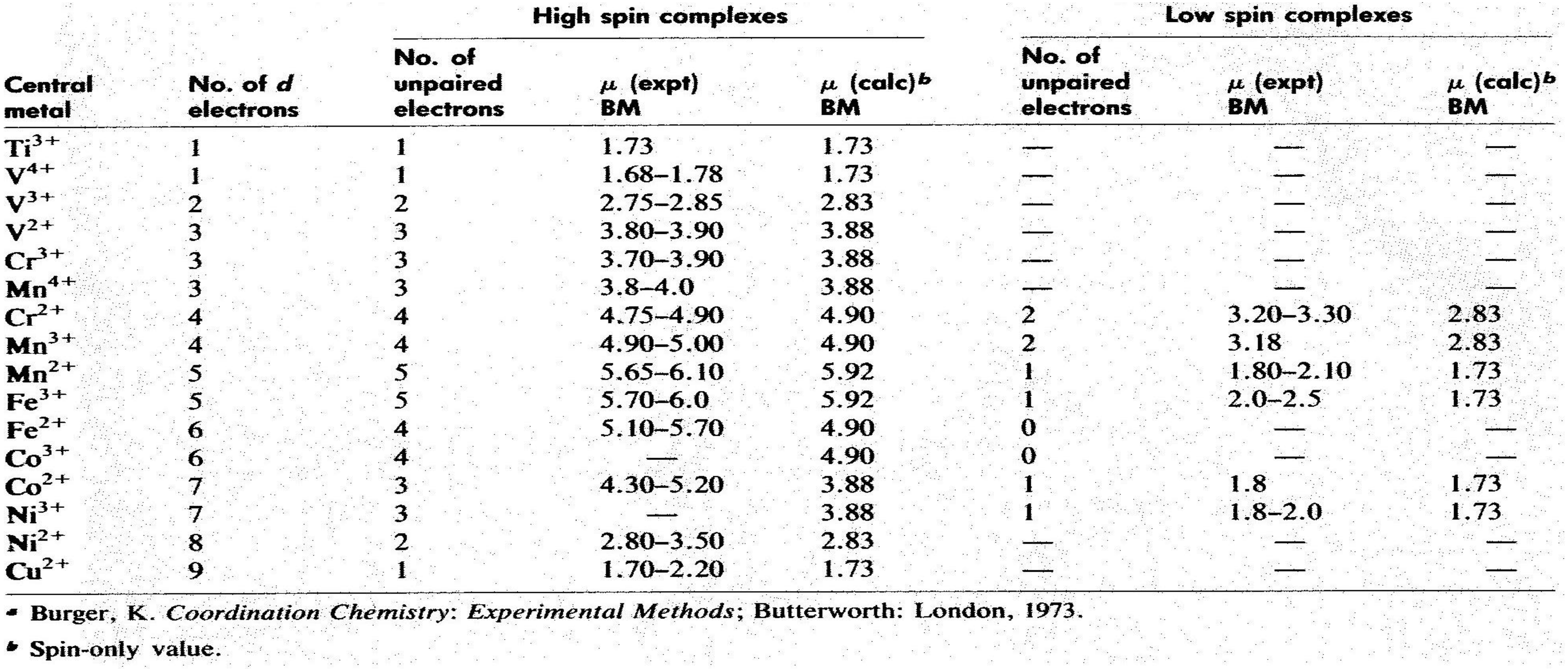
Cations[b]		**Anions**	
Li^+	−1.0	F^-	−9.1
Na^+	−6.8	Cl^-	−23.4
K^+	−14.9	Br^-	−34.6
Rb^+	−22.5	I^-	−50.6
Cs^+	−35.0	NO_3^-	−18.9
Tl^+	−35.7	ClO_3^-	−30.2
NH_4^+	−13.3	ClO_4^-	−32.0
Hg^{2+}	−40.0	CN^-	−13.0
Mg^{2+}	−5.0	NCS^-	−31.0
Zn^{2+}	−15.0	OH^-	−12.0
Pb^{2+}	−32.0	SO_4^{2-}	−40.1
Ca^{2+}	−10.4	O^{2-}	−12.0
Neutral Atoms			
H	−2.93	As(III)	−20.9
C	−6.00	Sb(III)	−74.0
N (ring)	−4.61	F	−6.3
N (open chain)	−5.57	Cl	−20.1
N (imide)	−2.11	Br	−30.6
O (ether or alcohol)	−4.61	I	−44.6
O (aldehyde or ketone)	−1.73	S	−15.0
P	−26.3	Se	−23.0
As(V)	−43.0		
Some Common Ligands			
H_2O	−13	$C_2O_4^{2-}$	−25
NH_3	−18	acetylacetonate	−52
C_2H_4	−15	pyridine	−49
CH_3COO^-	−30	bipyridyl	−105
$H_2NCH_2CH_2NH_2$	−46	*o*-phenanthroline	−128
Constitutive Corrections			
C=C	5.5	N=N	1.8
C=C—C=C	10.6	C=N—R	8.2
C≡C	0.8	C—Cl	3.1
C in benzene ring	0.24	C—Br	4.1

[a] Carlin, R. L. *Magnetochemistry*; Springer-Verlag: New York, 1986; p 3.

[b] The inner core diamagnetism of the first-row transition metals can be taken as approximately -13×10^{-6} (cgs units) mol^{-1}.

How do we interpret the results?

1. We can compare the magnetic moment with literature values for that ion.
2. We can decide if the expected oxidation state of the metal matches.
3. We can decide what the geometry of the complex is
4. We can decide if the complex is high spin or low spin
5. We can decide if the ligand(s) is/are weak or strong field



		High spin complexes			Low spin complexes		
Central metal	No. of *d* electrons	No. of unpaired electrons	μ (expt) BM	μ (calc)[b] BM	No. of unpaired electrons	μ (expt) BM	μ (calc)[b] BM
Ti^{3+}	1	1	1.73	1.73	—	—	—
V^{4+}	1	1	1.68–1.78	1.73	—	—	—
V^{3+}	2	2	2.75–2.85	2.83	—	—	—
V^{2+}	3	3	3.80–3.90	3.88	—	—	—
Cr^{3+}	3	3	3.70–3.90	3.88	—	—	—
Mn^{4+}	3	3	3.8–4.0	3.88	—	—	—
Cr^{2+}	4	4	4.75–4.90	4.90	2	3.20–3.30	2.83
Mn^{3+}	4	4	4.90–5.00	4.90	2	3.18	2.83
Mn^{2+}	5	5	5.65–6.10	5.92	1	1.80–2.10	1.73
Fe^{3+}	5	5	5.70–6.0	5.92	1	2.0–2.5	1.73
Fe^{2+}	6	4	5.10–5.70	4.90	0	—	—
Co^{3+}	6	4	—	4.90	0	—	—
Co^{2+}	7	3	4.30–5.20	3.88	1	1.8	1.73
Ni^{3+}	7	3	—	3.88	1	1.8–2.0	1.73
Ni^{2+}	8	2	2.80–3.50	2.83	—	—	—
Cu^{2+}	9	1	1.70–2.20	1.73	—	—	—

[a] Burger, K. *Coordination Chemistry: Experimental Methods*; Butterworth: London, 1973.

[b] Spin-only value.

Summary

1. **Magnetic moments are used to determine the spin state (high spin or low spin).**

2. **Octahedral complexes can be either high spin or low spin.**

3. **Tetrahedral complexes can only be high spin.**

4. **The magnitude of the orbital contribution differ for tetrahedral and octahedral ,it is greater for octahedral than for tetrahedral.**

Therefore ,we can distinguish between tetrahedral and octahedral.

Tetrahedral; 4.30 – 4.72 B.M.

Octahedral; 4.90 – 5.40 B.M.

https://www.youtube.com/watch?v=SMcJskQhaW0