

UNIVERSITY OF DUBLIN  
TRINITY COLLEGE

Faculty of Engineering, Mathematics and Science

Schools of Chemistry & Physics

Moderatorship Examination

Trinity Term 2015

Physics and Chemistry of Advanced Materials

Comprehension and Problem-Solving Paper

Friday 1<sup>st</sup> May 2015

SNIAM PHYS

09.30-12.30

Paper Coordinator: Prof. Duesberg

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Complete the comprehension exercise in **Section A**  
and **answer 6** questions from **Section B**

**Section A** accounts for 40% and **Section B** accounts for 60%

**Please use separate answer books for each question**

Tables of physical constants and relative atomic masses and a periodic table are attached.

Spectroscopic tables, character tables, Mathematical Tables (Old) or Formulae and Tables (New) and graph paper are available from the invigilators, if required.

Non-programmable calculators are permitted for this examination – please indicate the make and model of your calculator on each answer book used.

## SECTION A

## Question 1

- (a) Summarise the science article below in your own words (approximately one page).

[10 marks]

- (b) Where does the high spatial resolution in noncontact AFM arise from? Why is noncontact AFM useful at the atomic level?

[8 marks]

- (c) Are the forces interacting between the CO molecule on the AFM tip directionally dependant? Why/Why not? Explain your reasoning.

[10 marks]

- (d) The two CO molecules involved are attracted to each other at long distances and repel each other at close ones. This attraction can be modelled as a Morse Potential as follows:

$$E_M = E_B \left( -2 \exp \left[ -\frac{r - \sigma}{\lambda} \right] + \exp \left[ -2 \frac{r - \sigma}{\lambda} \right] \right)$$

$E_M$  is the Morse potential energy, the bond energy  $E_B = 8.4\text{meV}$ ,  $\sigma$  is the equilibrium distance and the decay length  $\lambda = 47\text{pm}$ .  $r$  is the core-core distance between the two oxygen atoms.

- (i) Using the equation given, find an expression in terms of  $r$  for the force of interaction between the two oxygen atoms
- (ii) Given an equilibrium distance of 385 pm, find the force of interaction in Newtons at a distance of 500 pm. Comment on the magnitude of this force.

[12 marks]

# CO Meets CO, One at a Time

Miquel Salmeron

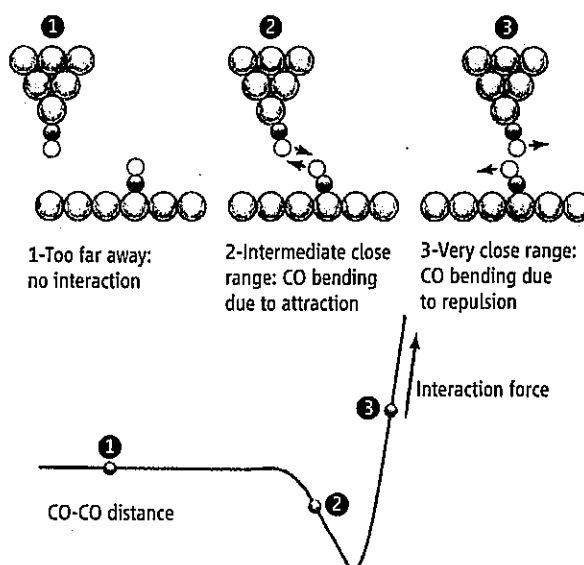
In his 1959 lecture, "There is plenty of room at the bottom" (1), Richard Feynman challenged scientists to build microscopes that could be used to manipulate atoms one by one. Twenty-five years later, the scanning tunneling microscope (STM) was invented (2), enabling individual atoms to be dragged to specific locations in a smooth surface (3). The atomic force microscope (AFM) (4) allowed even more sophisticated manipulations of atoms and molecules. At first sight, the importance of these feats may appear to be of an academic nature, but the wider implications in nanotechnology, which aims to manipulate matter at the atomic level to produce new materials, soon became clear. On page 1120 of this issue, Weymouth *et al.* (5) measure the forces between two single CO molecules, an example of the type of fundamental understanding that can be obtained with atomic force microscopy.

In an AFM, a sharp tip is mounted on a vibrating cantilever like that of the tuning fork used in the humble wrist watch. When the AFM is operated in noncontact mode (in which the sharp tip does not directly touch the surface), the last atom in its tip feels the tiny forces associated with attraction to and repulsion from other nearby atoms or molecules. These forces are the same as those between two atoms that are in the process of forming a chemical bond; their strength decays exponentially at distances comparable to the size of the atom.

With the noncontact AFM, one can obtain images of individual atoms and of atoms

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within molecules with picometer resolution ( $10^{-12}$  m). It can also distinguish the component atoms inside the molecules by mapping the electron clouds of the chemical bonds, as shown recently in detailed images of penta-cene, a planar molecule with five benzene-like rings (6). In this work, Gross *et al.* followed Eigler's pioneering work (7) by attaching an atom or molecule to the end of the tip; this atom or molecule is then used to image the surface. This tip engineering removes the uncertainty of the atomic structure of the tip apex, a problem that plagues more standard STM and AFM imaging.



**Close approach.** Weymouth *et al.* attached a CO molecule to the AFM tip and then measured the changes in interaction energy as the tip came near a surface-bound CO molecule.

An atomic force microscope is used to measure the molecular forces between two carbon monoxide (CO) molecules.

The high spatial resolution achieved in noncontact AFM results from the exquisite sensitivity of the vibration frequency of the quartz tuning fork, the same reason that quartz watches keep time so accurately. Tiny changes in this frequency due to atom-atom interactions can then be used to obtain atomically resolved images when the tip is rastered over a surface. More important, the measured frequency shifts can be used for a quantitative determination of the forces at play.

Weymouth *et al.* do precisely this. They measure the shifts in the tuning-fork frequency when a CO molecule attached to the tip end is brought close to another CO molecule adsorbed on the surface of a copper crystal. As the oxygen atoms of the molecules approach each other, they first attract and later repel when their electron clouds overlap too much (see the figure). From the frequency shifts, the authors obtain a map of interaction energy between the oxygen atoms in the molecules. The departure of the repulsive part of the force from the expected curve shows that at close contacts, the molecules bend to avoid each other (see the figure).

To investigate the stiffness of this bending motion in detail, the authors next measured the frequency shift when the tuning fork and its

## References and Notes

1. For a transcript of the lecture, see [www.its.caltech.edu/~feynman/plenty.html](http://www.its.caltech.edu/~feynman/plenty.html).
2. G. Binnig, H. Rohrer, Ch. Gerber, E. Weibel, *Appl. Phys. Lett.* **40**, 178 (1982).
3. D. M. Eigler, E. K. Schweizer, *Nature* **344**, 524 (1990).
4. G. Binnig, C. F. Quate, C. Gerber, *Phys. Rev. Lett.* **56**, 930 (1986).
5. A. J. Weymouth, T. Hofmann, F. J. Giessibl, *Science* **343**, 1120 (2014); 10.1126/science.1249502.
6. L. Gross, F. Mohn, N. Moll, P. Liljeroth, G. Meyer, *Science* **325**, 1110 (2009).
7. D. M. Eigler, C. P. Lutz, W. E. Rudge, *Nature* **352**, 600 (1991).
8. Y. Sugimoto *et al.*, *Nature* **446**, 64 (2007).

## PERSPECTIVES

attached CO molecule oscillate horizontally while approaching another CO molecule on the surface. By doing this at different heights over the Cu surface, the authors were able to obtain a complete map of the forces and energies between the CO molecules.

As the result reported by Weymouth *et al.* show, noncontact AFM is a crucial tool in the quest to image atoms and molecules at ever higher resolution and to understand the origin of the forces that keep them together. From the measured forces, it is possible to identify the nature of the atoms (8) and to deduce their interaction energies. Furthermore, it opens the way for studying chemical reactions at the

individual atom or molecule level. For example, one could choose a particular site on the surface of a catalyst and position an atom or molecule there, using the tip as "tweezers." By bringing another atom or molecule near to the first from various directions and at various distances and measuring the resulting forces, one could determine whether a reaction occurs and what the products are. In another scenario, the technique could be used to construct novel molecules by bringing the component atoms to the chosen locations one at a time. Such experiments are already happening in the laboratories of researchers. The possibilities are endless.

## SECTION B

**Question 2**

The statistical view of diffusion is a random walk process. Write down the expression for the root mean square distance  $\delta$  travelled by a molecule in terms of the diffusion coefficient  $D$  and the time  $t$ . Assuming that a small molecule in an aqueous solution has a diffusion coefficient  $D \cong 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ , how far would such a molecule diffuse in

- (i) 1 second
- (ii) one day?

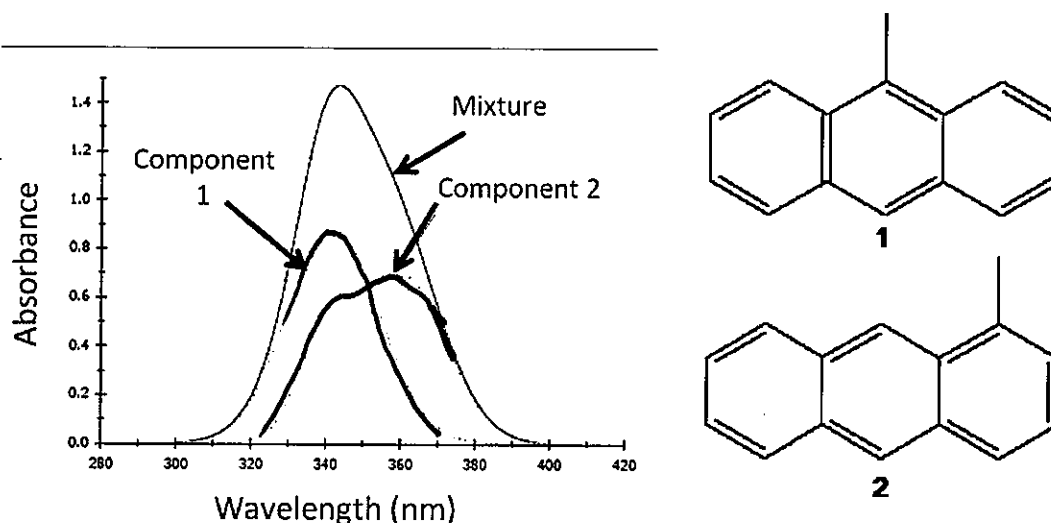
[10 marks]

**Question 3**

A fisherman takes an action photograph of a leaping trout, which is 10 m from the camera. If spots on the trout are separated by 4 mm, what is the minimum camera aperture at which the spots are resolved in the photograph? A standard camera aperture is 25 mm in diameter. What is the maximum distance at which the trout's spots could be resolved using this aperture?

[10 marks]

## Question 4



The UV absorption spectra of the organic pollutants, 9-methylanthracene (**1**) and 1-methylanthracene (**2**) in cyclohexane are shown above. The following molar absorption coefficients were determined:  $\epsilon = 145,000 \text{ L mol}^{-1} \text{ cm}^{-1}$  ( $\lambda_{\text{abs}} = 340 \text{ nm}$ ) and  $\epsilon = 90,000 \text{ L mol}^{-1} \text{ cm}^{-1}$  ( $\lambda_{\text{abs}} = 360 \text{ nm}$ ) for compound **1** and  $\epsilon = 85,000 \text{ L mol}^{-1} \text{ cm}^{-1}$  ( $\lambda_{\text{abs}} = 340 \text{ nm}$ ) and  $\epsilon = 110,000 \text{ L mol}^{-1} \text{ cm}^{-1}$  ( $\lambda_{\text{abs}} = 360 \text{ nm}$ ) for compound **2**.

The UV absorption spectrum of sample known to contain a mixture of the two compounds was measured and found to have an absorbance of 1.4 at 340 nm and 1.05 at 360 nm. All measurements were performed with a pathlength of 1 cm.

Assuming Beer's law is valid and that there is no contribution from other contaminants to the spectrum, use this information to determine the concentration of compounds **1** and **2** in the mixture. Show your working.

[10 marks]

## Question 5

A proton collides with a Hydrogen atom in its ground state and excites it to the  $n=4$  state. How much energy was given to the Hydrogen atom in this inelastic collision? The Rydberg energy is  $-13.6 \text{ eV}$ .

[10 marks]

**Question 6**

Given the following information calculate the length and force constant of the bond in  $\text{H}^{35}\text{Cl}$

- (a) The microwave spectrum of  $\text{H}^{35}\text{Cl}$  is comprised of a series of equally spaced lines separated by  $6.26 \times 10^{11}$  Hz
- (b) The infrared spectrum of  $\text{H}^{35}\text{Cl}$  consists of an intense line at  $2886 \text{ cm}^{-1}$

[10 marks]

**Question 7**

The Mariana trench is located in the Pacific Ocean. Its deepest point is eleven kilometers below the surface. A steel ball of volume  $0.2 \text{ m}^3$  is dropped into this deepest point. What is the change in the volume of the ball when it reaches the bottom? The bulk modulus of steel is  $1.4 \times 10^{11} \text{ N m}^{-2}$ . Make an estimate of the change in volume that would occur if the ball was made of nylon. The bulk modulus of nylon is  $4.1 \times 10^9 \text{ N m}^{-2}$ .

[10 marks]

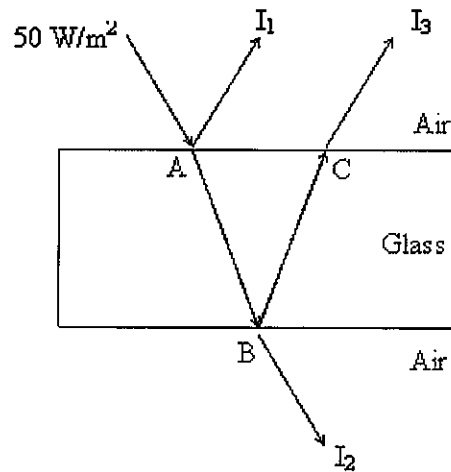
**Question 8**

- (a) Derive Bragg's Law and define the terms used.
- (b) The crystal structure of  $\text{SrTiO}_3$  is cubic (space group  $\text{Pm}\bar{3}\text{m}$ ). Given that the unit cell edge is  $3.90 \text{ \AA}$ , calculate the expected  $2\theta$  positions of the first two peaks in the diffraction pattern assuming the radiation is  $\text{Cu K}\alpha$  ( $\lambda = 1.54 \text{ \AA}$ ).
- (c) Assuming the diffractometer radius is  $R = 225 \text{ mm}$  and the sample was displaced by  $0.1 \text{ mm}$ , calculate the how much each peak will shift and thereby estimate the consequent error in the cell edges.

[10 marks]

**Question 9**

Light of intensity  $50 \text{ W m}^{-2}$  is incident on a glass windowpane ( $n = 1.5$ ), with rays approximately perpendicular to the surface, as show in figure below. Find the intensity  $I_1$ ,  $I_2$ , and  $I_3$ .



**Hint:**

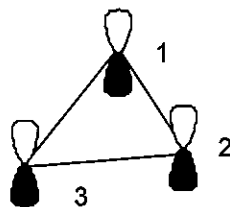
$$R_s = \left| \frac{n_1 \cos \theta_i - n_2 \cos \theta_t}{n_1 \cos \theta_i + n_2 \cos \theta_t} \right|^2 = \left| \frac{n_1 \cos \theta_i - n_2 \sqrt{1 - \left(\frac{n_1}{n_2} \sin \theta_i\right)^2}}{n_1 \cos \theta_i + n_2 \sqrt{1 - \left(\frac{n_1}{n_2} \sin \theta_i\right)^2}} \right|^2,$$

$$R_p = \left| \frac{n_1 \cos \theta_t - n_2 \cos \theta_i}{n_1 \cos \theta_t + n_2 \cos \theta_i} \right|^2 = \left| \frac{n_1 \sqrt{1 - \left(\frac{n_1}{n_2} \sin \theta_i\right)^2} - n_2 \cos \theta_i}{n_1 \sqrt{1 - \left(\frac{n_1}{n_2} \sin \theta_i\right)^2} + n_2 \cos \theta_i} \right|^2.$$

**[10 marks]**

**Question 10**

The three  $p$ -atomic orbitals contributing to the  $\pi$ -molecular orbitals in the cyclo-propenyl cation are depicted below.:



One of the  $\pi$ -molecular orbitals is given in the Hückel approximation by

$$\psi_2 = \frac{1}{\sqrt{2}}(\phi_2 - \phi_3)$$

Determine both remaining  $\pi$ -orbitals assuming the molecular shape is that of a perfectly equilateral triangle.

**[10 marks]**

**Question 11**

Using your knowledge of the energy-level spacing for a 1-dimensional particle in an infinite potential box, as well as the energy level spacing of a 1-dimensional harmonic oscillator, predict whether the energy levels of the particle confined to the following potentials converge or diverge. That is, as the energy gets larger does the energy spacing between states increase or decrease? Justify your answer.

- (a) A particle in a potential  $V(x) = |x|$
- (b) A particle in a potential  $V(x) = ax^4$  where  $a > 0$ .

**[10 marks]**



**Question 12**

The following data was collected for CO adsorption onto {111} surface of two different transition metals at two different coverages. Account for the data in the table below, sketch a possible surface unit cell for each surface and name the overlayer structures.

Surface	Surface Coverage ( $\theta$ )	Vibrational frequency	Work function change relative to clean surface
A	0.25	2088 $\text{cm}^{-1}$	-0.75 eV
B	0.33	1846 $\text{cm}^{-1}$	+0.75 eV

**[10 marks]****Question 13**

A square loop of aluminium wire with sides of length of 25 cm, carries a current of 20 A and is oriented perpendicular to a magnetic field of 1.5 T. Determine the minimum diameter of the wire such that it does not fracture due to the tension.

[Tensile strength of aluminium =  $200 \times 10^6 \text{ N m}^{-2}$ ]

**[10 marks]**

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Tables of constants from the Schools of Chemistry and Physics are provided below. You may use either but please pay attention to the occasional difference in Units employed.

**SCHOOL OF PHYSICS**

Electron rest mass	$m_e$	$9.11 \times 10^{-31} \text{ kg}$
Proton rest mass	$M_p$	$1.67 \times 10^{-27} \text{ kg}$
Electronic charge	$e$	$1.60 \times 10^{-19} \text{ C}$
Speed of light in free space	$c$	$3.00 \times 10^8 \text{ m s}^{-1}$
Planck's constant	$h$	$6.63 \times 10^{-34} \text{ J s}$
	$h/2\pi = \hbar$	$1.05 \times 10^{-34} \text{ J s}$
Boltzmann's constant	$k$	$1.38 \times 10^{-23} \text{ J K}^{-1}$
Molar gas constant	$R$	$8.31 \times 10^3 \text{ JK}^{-1}\text{kmol}^{-1}$
Avogadro's number	$N_A$	$6.02 \times 10^{26} \text{ kmol}^{-1}$ $= 6.02 \times 10^{23} \text{ mol}^{-1}$
Standard molar volume		$22.4 \times 10^{-3} \text{ m}^3$
Bohr magneton	$\mu_B$	$9.27 \times 10^{-24} \text{ A m}^2$ <u>OR</u> $\text{J T}^{-1}$
Nuclear magneton	$\mu_N$	$5.05 \times 10^{-27} \text{ A m}^2$ <u>OR</u> $\text{J T}^{-1}$
Bohr radius	$a_0$	$5.29 \times 10^{-11} \text{ m}$
Fine structure constant		
$e^2/(4\pi\epsilon_0\hbar c)$	$= \alpha$	$(1/137)^{-1}$
Rydberg's constant	$R_\infty$	$1.10 \times 10^7 \text{ m}^{-1}$
Stefan's constant	$\sigma$	$5.67 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$
Gravitational constant	$G$	$6.67 \times 10^{-11} \text{ N m}^2 \text{ kg}^{-2}$
Proton magnetic moment	$\mu_p$	$2.79 \mu_N$
Neutron magnetic moment	$\mu_n$	$-1.91 \mu_N$
Permeability of free space	$\mu_0$	$4\pi \times 10^{-7} \text{ H m}^{-1}$
Permittivity of free space	$\epsilon_0$	$8.85 \times 10^{-12} \text{ F m}^{-1}$
1 electron volt	$eV$	$1.60 \times 10^{-19} \text{ J}$
1 unified atomic mass unit ( $^{12}\text{C}$ scale)		$1.66 \times 10^{-27} \text{ kg} = 931$
$\text{MeV}/c^2$		
Wavelength of 1 eV photon		$1.24 \times 10^{-6} \text{ m}$
1 atmosphere		$1.01 \times 10^5 \text{ N m}^{-2}$
Standard acceleration due to gravity		$10 \text{ m s}^{-2}$
Free space impedance $Z_0$		$377 \Omega$

## School of Chemistry

**Constants**

Gas Constant	$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ ( $R = 8.206 \times 10^{-2} \text{ L atm K}^{-1} \text{ mol}^{-1}$ )
Boltzmann's Constant	$k_B = 1.381 \times 10^{-23} \text{ J K}^{-1}$
Planck's Constant	$h = 6.626 \times 10^{-34} \text{ J s}$ $\hbar = h/2\pi = 1.055 \times 10^{-34} \text{ J s}$
Velocity of light	$c = 2.998 \times 10^8 \text{ m s}^{-1}$
Charge of electron	$e = -1.602 \times 10^{-19} \text{ C}$
Rest mass of electron	$m_e = 9.109 \times 10^{-31} \text{ kg}$
Rest mass of proton	$m_p = 1.673 \times 10^{-27} \text{ kg}$
Atomic Mass Unit	$1 \text{ u} = 1.66054 \times 10^{-27} \text{ kg}$
Vacuum permittivity	$\epsilon_0 = 8.854 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$
Vacuum permeability	$\mu_0 = 4\pi \times 10^{-7} \text{ J s}^2 \text{ C}^{-2} \text{ m}^{-1}$
Bohr magneton	$\beta = 9.274 \times 10^{-24} \text{ J T}^{-1}$
Nuclear magneton	$\beta_n = 5.051 \times 10^{-27} \text{ J T}^{-1}$
Rydberg constant	$R_\infty = 2.178 \times 10^{-18} \text{ J} = 1.097 \times 10^5 \text{ cm}^{-1}$
Avogadro's constant	$N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$
Faraday constant	$F = N_A e = 9.648 \times 10^4 \text{ C mol}^{-1}$
Bohr radius	$a_0 = 5.292 \times 10^{-11} \text{ m}$
Molar volume at S.T.P.	$M_V = 22.414 \text{ dm}^3 \text{ mol}^{-1}$

**Conversion factors etc.**

$$1 \text{ eV} = 1.602 \times 10^{-19} \text{ J} = 9.648 \times 10^4 \text{ J mol}^{-1}$$

$$1 \text{ cm}^{-1} = 1.986 \times 10^{-23} \text{ J} = 11.96 \text{ J mol}^{-1} = 1.240 \times 10^{-4} \text{ eV}$$

$$1 \text{ \AA} = 0.1 \text{ nm} = 10^{-10} \text{ m}$$

$$1 \text{ standard atmosphere} = 1.013 \times 10^5 \text{ N m}^{-2} \text{ (Pa)} = 760 \text{ torr} = 1013 \text{ mbar}$$

$$1 \text{ L} = 1 \text{ dm}^3 = 10^{-3} \text{ m}^3$$

$$1 \text{ Debye (D)} = 3.336 \times 10^{-30} \text{ C m}$$

$$1 \text{ calorie} = 4.184 \text{ J}$$

### Approximate values of relative atomic masses

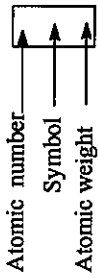
(Values in brackets are mass numbers of longest lived isotopes).

Ac (227)	Ge 72.6	Po (209)
Ag 107.9	H 1.0	Pr 140.9
Al 27.0	He 4.0	Pt 195.1
Am (243)	Hf 178.5	Pu (244)
Ar 40.0	Hg 200.6	Ra (226)
As 74.9	Ho 164.9	Rb 85.5
At (210)	I 126.9	Re 186.2
Au 197.0	In 114.8	Rh 102.9
B 10.8	Ir 192.2	Rn (222)
Ba 137.3	K 39.1	Ru 101.1
Be 9.0	Kr 83.8	S 32.0
Bi 209.0	La 138.9	Sb 121.8
Bk (247)	Li 6.9	Sc 45.0
Br 79.9	Lu 175.0	Se 79.0
C 12.0	Lw (257)	Si 28.1
Ca 40.1	Md (258.1)	Sm 150.4
Cd 112.4	Mg 24.3	Sn 118.7
Ce 140.1	Mn 54.9	Sr 87.6
Cf (242.1)	Mo 95.9	Ta 180.9
Cl 35.5	N 14.0	Tb 158.9
Cm (247)	Na 23.0	Tc (97.9)
Co 58.9	Nb 92.9	Te 127.6
Cr 52.0	Nd 144.2	Tl 204.4
Cs 132.9	Ne 20.2	Th 232.0
Cu 63.5	Ni 58.7	Ti 47.9
Dy 162.5	No (259.1)	Tm 168.9
Er 167.3	Np (237)	U 238.0
Es (252.1)	O 16.0	V 50.9
Eu 152.0	Os 190.2	W 183.9
F 19.0	P 31.0	Xe 131.3
Fe 55.9	Pa (231)	Y 88.9
Fm (257)	Pb 207.2	Yb 173.0
Fr (223)	Pd 106.4	Zn 65.4
Ga 69.7	Pm (145)	Zr 91.2
Gd 157.3		

### The Periodic Table of the Elements

																		18																	
													13	14	15	16	17	18																	
1	2															5	6	7	8	9	10	11	12	13	14	15	16	17	18						
1	H	He														B	C	N	O	F	Ne														
3	Li	Be														5	6	7	8	9	10	11	12	13	14	15	16	17	18						
3	Li	Be														5	6	7	8	9	10	11	12	13	14	15	16	17	18						
11	Na	Mg	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18																	
11	Na	Mg	3d, 4d, 5d														13	14	15	16	17	18													
19	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	31	32	33	34	35	36																	
19	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	31	32	33	34	35	36																	
37	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	49	50	51	52	53	54																	
37	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	49	50	51	52	53	54																	
55	Cs	Ba	#La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	81	82	83	84	85	86																	
55	Cs	Ba	#La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	81	82	83	84	85	86																	
87	Fr	Ra	*Ac														81	82	83	84	85	86													
87	Fr	Ra	*Ac														81	82	83	84	85	86													

Key



( ) mass numbers of most stable isotope

### # LANTHANUM SERIES

58	Ce	Pr	Nd	Pm	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
140.12	140.9077	144.24	(145)	150.36	157.25	158.9254	162.50	164.9304	167.26	168.9342	173.04	174.967

### \* ACTINIUM SERIES

90	Th	Pa	U	Np	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
232.0381	231.0359	238.0389	237.0482	(243)	(243)	(247)	(247)	(242.1)	(254)	(257)	(258.1)	(259.1)	(260)