Topics in the June 2012 Exam Paper for CHEM1903

Click on the links for resources on each topic.

2012-J-2:

- Bonding in H_2 - MO theory
- Bonding in O_2, N_2, C_2H_2, C_2H_4 and CH_2O

2012-J-3:

- Atomic Electronic Spectroscopy
- Bonding in O_2, N_2, C_2H_2, C_2H_4 and CH_2O

2012-J-4:

- Nuclear and Radiation Chemistry

2012-J-5:

- Nuclear and Radiation Chemistry

2012-J-6:

- Lewis Structures
- VSEPR

2012-J-7:

- Thermochemistry

2012-J-8:

- First and Second Law of Thermodynamics

2012-J-9:

- Polar Bonds
- Ionic Bonding

2012-J-10:

- Chemical Equilibrium

2012-J-11:

- Electrochemistry
- Batteries and Corrosion

2221(a)

THE UNIVERSITY OF SYDNEY

CHEMISTRY 1A (ADVANCED) - CHEM1901

CHEMISTRY 1A (SPECIAL STUDIES PROGRAM) - CHEM1903

CONFIDENTIAL

FIRST SEMESTER EXAMINATION

JUNE 2012 **TIME ALLOWED: THREE HOURS**

GIVE THE FOLLOWING INFORMATION IN BLOCK LETTERS

FAMILY NAME		**SID NUMBER**	
OTHER NAMES		**TABLE NUMBER**	

INSTRUCTIONS TO CANDIDATES

- All questions are to be attempted. There are 20 pages of examinable material.
- Complete the written section of the examination paper in **INK.**
- Read each question carefully. Report the appropriate answer and show all relevant working in the space provided.
- The total score for this paper is 100. The possible score per page is shown in the adjacent tables.
- Each new short answer question begins with a •.
- Only non-programmable, University-approved calculators may be used.
- Students are warned that credit may not be given, even for a correct answer, where there is insufficient evidence of the working required to obtain the solution.
- Numerical values required for any question, standard electrode reduction potentials, a Periodic Table and some useful formulas may be found on the separate data sheets.
- Pages 17, 20 and 24 are for rough working only.

OFFICIAL USE ONLY

Multiple choice section

	Marks	
Pages	Max	Gained
2-10	31	

Short answer section

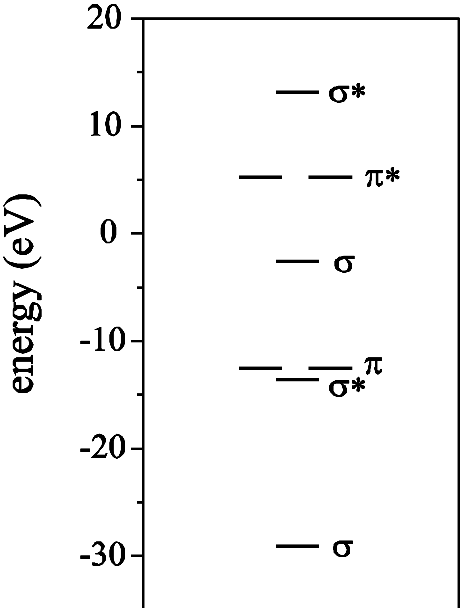
	Marks			
Page	Max	Gained		Marker
11	5			
12	6			
13	4			
14	8			
15	8			
16	6			
18	4			
19	6			
21	9			
22	6			
23	7			
Total	69			
Check Total				

Marks
5

- C_2 is a reaction intermediate observed in flames, comets, circumstellar shells and the interstellar medium. In 2011, a new state of C_2 was observed with 4 parallel spins.

How many *valence* electrons are there in C_2?

Complete the calculated MO diagram for the lowest energy state of C_2 *with 4 parallel spins* by inserting the appropriate number of electrons into the appropriate orbitals.



What is the bond order of this state of C_2?

Is this state paramagnetic? Give reasoning.

What is the bond order of the ground state of C_2?

Marks
6

- An "excimer laser" is a type of ultraviolet laser used for lithography, micromachining and eye surgery. In one type of laser, an electrical discharge through HCl and Xe in a helium buffer gas yields metastable XeCl molecules, described like an ion pair. These then emit 308 nm light and dissociate into Xe and Cl atoms.

element	Ionisation energy / kJ mol^{-1}	Electron affinity / kJ mol^{-1}
Xe	1170.4	–
Cl	1251.1	–349

What energy, in eV, is required to convert a pair of Xe and Cl atoms into Xe^+ and Cl^- ions?

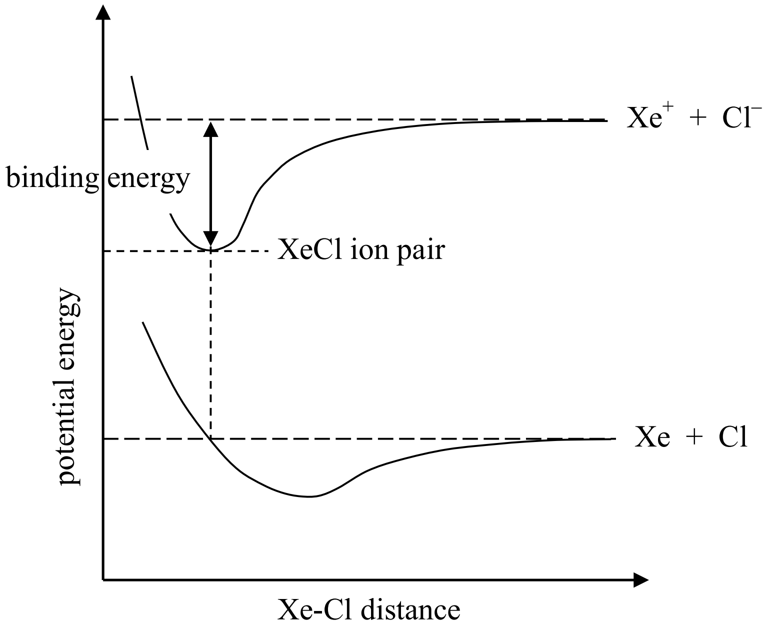
Answer:

What energy (in eV) is released when the XeCl molecules emit ultraviolet light?

Answer:

THIS QUESTION CONTINUES ON THE NEXT PAGE.

Marks
4



What is the binding energy (in J) of the XeCl ion pair?

Answer:

If the binding energy is electrostatic, what is the approximate equilibrium bond length of XeCl if the binding energy is given by the Coulomb formula: $E = \frac{q_1 q_2}{4\pi\varepsilon_0 r}$?

Answer:

Marks
8

- The generation of energy in a nuclear reactor is largely based on the fission of either ^{235}U or ^{239}Pu. The fission products include every element from zinc through to the *f*-block. Explain why most of the radioactive fission products are β-emitters.

Much of the fission yield is concentrated in two peaks, one in the second transition row and the other later in the periodic table. Identify the missing "sister" products of the following daughter nuclides of ^{235}U by writing balanced nuclear equations. The fission reactions are triggered by the absorption of one neutron, and release three neutrons upon disintegration of the short-lived ^{236}U nucleus.

^{141}Ba	
^{95}Sr	

Many of the fission products are short lived, and spent fuel rods are eventually contaminated by longer-lived species. The radioactivity of spent fuel can be modelled simply by the exponential decay of the ^{137}Cs and ^{90}Sr. The % yields and half lives of these nuclides are given in the table.

nuclide	%Yield *per fission event*	Half-life (years)
^{90}Sr	4.505	28.9
^{137}Cs	6.337	30.23

After use, nuclear fuel rods are stored in ponds of cooling water, awaiting safe disposal. If 3 % of the mass of used fuel rods consists of fission products of ^{235}U and ^{239}Pu, what percentage of the mass is made up by each of these nuclides?

^{90}Sr:	^{137}Cs:

THIS QUESTION CONTINUES ON THE NEXT PAGE.

Marks
8

What are the specific activities of ^{90}Sr and ^{137}Cs in Bq g^{-1}?

^{90}Sr:

^{137}Cs:

Assuming the majority of the activity of a spent fuel rod to be due to these nuclides, what will be the activity of a 1 tonne fuel rod 100 years after placing it in the pond?

Answer:

Marks
6

- Complete the table below showing the Lewis structures and the predicted shapes of the following species.

Formula	Lewis Structure	Approximate F-X-F bond angle(s)	Name of molecular shape
NF_3			
XeF_3^+			
XeF_4			
$XeOF_4$			

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY

Marks
4

- When 20.0 mL of 0.250 M $Ba(OH)_2$ at 47.5 °C is added to a constant pressure ("coffee cup") calorimeter containing 200.0 mL of 0.500 M H_2SO_4 also at 47.5 °C, a white precipitate is formed. The final temperature of the solution is 46.4 °C. Given that the enthalpy of neutralisation of $H^+(aq)$ and $OH^-(aq)$ is -56.5 kJ mol^{-1}, and assuming that the specific heat capacity and density of all solutions involved are the same as that of pure water ($c = 4.184$ J K^{-1} g^{-1} and $\rho = 1.000$ g mL^{-1}), calculate the enthalpy of solution of $BaSO_4$ in kJ mol^{-1}.

Answer:

Marks
6

- Explain the following phenomena.

(a) When O_2 dissolves in water at room temperature, the total entropy of the system decreases.

(b) When $MgSO_4$ is dissolved in water, there is a very small but measurable decrease in volume.

(c) A crystal (*e.g.* of NaCl) in its lowest energy configuration (thermodynamic ground state) will always contain defects at finite temperatures.

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY

Marks

- Explain, with the aid of a diagram labelling all the key components, how sodium stearate ($C_{17}H_{35}COONa$) can stabilise long-chain non-polar hydrocarbons ("grease") in water.

3

- Consider the complex $K_4[Mn(CN)_6]$. Describe and contrast the origin, strength and directionality of the chemical bonds in this compound (a) between C and N; (b) between the manganese and cyanide ions; and (c) between the complex and the potassium counterions.

6

Marks
6

- Equal volumes of carbon monoxide and hydrogen gas are introduced into a sealed 4.5 L flask at 1200 K and the following reaction occurs.

$$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$$

Sometime later, total pressure in the flask is 46.4 atm. Calculate the total amount of gas (in mol) in the flask at this later time.

Answer:

When the total pressure in the flask is 46.4 atm, the flask contains 0.22 mol of CH_4. Calculate the amount of $H_2(g)$ (in mol) that was initially introduced into the flask.

Answer:

In a separate experiment, it is determined that the reaction is in equilibrium when the same 4.5 L flask contains 0.18 mol of CH_4, 0.24 mol of H_2O, 0.82 mol of CO and 0.65 mol of H_2 at 1200 K. Was the reaction at equilibrium in the previous part of this question? Show all working.

Answer: YES / NO

Marks
7

- A voltaic cell is set up at 298 K based on the following half-cell reactions.

$$\mathrm{Pt^{2+}(aq)} + 2\mathrm{e^-} \rightleftharpoons \mathrm{Pt(s)} \qquad E^\circ = +1.18\ \mathrm{V}$$

$$\mathrm{Rh^{3+}(aq)} + 3\mathrm{e^-} \rightleftharpoons \mathrm{Rh(s)} \qquad E^\circ = +0.76\ \mathrm{V}$$

Write the overall chemical reaction that takes place in this cell.

Write the same reaction in shorthand voltaic cell notation**.**

Which metal electrode is acting as the cathode in this reaction?

Calculate the potential of this cell at 298 K, in which the concentration of $\mathrm{Pt^{2+}(aq)}$ is 0.0544 mmol $\mathrm{L^{-1}}$ and the concentration of $\mathrm{Rh^{3+}(aq)}$ is 0.0393 mmol $\mathrm{L^{-1}}$**.**

Answer:

2221(b) June 2012

CHEM1901 - CHEMISTRY 1A (ADVANCED)

CHEM1903 - CHEMISTRY 1A (SPECIAL STUDIES PROGRAM)

DATA SHEET

Physical constants

Avogadro constant, $N_A = 6.022 \times 10^{23}$ mol^{-1}

Faraday constant, $F = 96485$ C mol^{-1}

Planck constant, $h = 6.626 \times 10^{-34}$ J s

Speed of light in vacuum, $c = 2.998 \times 10^{8}$ m s^{-1}

Rydberg constant, $E_R = 2.18 \times 10^{-18}$ J

Boltzmann constant, $k_B = 1.381 \times 10^{-23}$ J K^{-1}

Permittivity of a vacuum, $\varepsilon_0 = 8.854 \times 10^{-12}$ C^2 J^{-1} m^{-1}

Gas constant, $R = 8.314$ J K^{-1} mol^{-1}

$= 0.08206$ L atm K^{-1} mol^{-1}

Charge of electron, $e = 1.602 \times 10^{-19}$ C

Mass of electron, $m_e = 9.1094 \times 10^{-31}$ kg

Mass of proton, $m_p = 1.6726 \times 10^{-27}$ kg

Mass of neutron, $m_n = 1.6749 \times 10^{-27}$ kg

Properties of matter

Volume of 1 mole of ideal gas at 1 atm and 25 °C = 24.5 L

Volume of 1 mole of ideal gas at 1 atm and 0 °C = 22.4 L

Density of water at 298 K = 0.997 g cm^{-3}

Conversion factors

1 atm = 760 mmHg = 101.3 kPa

0 °C = 273 K

1 L = 10^{-3} m^3

1 Å = 10^{-10} m

1 eV = 1.602×10^{-19} J

1 Ci = 3.70×10^{10} Bq

1 Hz = 1 s^{-1}

1 tonne = 10^3 kg

1 W = 1 J s^{-1}

Decimal fractions

Fraction	Prefix	Symbol
10^{-3}	milli	m
10^{-6}	micro	μ
10^{-9}	nano	n
10^{-12}	pico	p

Decimal multiples

Multiple	Prefix	Symbol
10^{3}	kilo	k
10^{6}	mega	M
10^{9}	giga	G

CHEM1901 - CHEMISTRY 1A (ADVANCED)

CHEM1903 - CHEMISTRY 1A (SPECIAL STUDIES PROGRAM)

Standard Reduction Potentials, E°

Reaction	$E°$ / V
$Co^{3+}(aq) + e^- \rightarrow Co^{2+}(aq)$	+1.82
$Ce^{4+}(aq) + e^- \rightarrow Ce^{3+}(aq)$	+1.72
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O$	+1.51
$Au^{3+}(aq) + 3e^- \rightarrow Au(s)$	+1.50
$Cl_2 + 2e^- \rightarrow 2Cl^-(aq)$	+1.36
$O_2 + 4H^+(aq) + 4e^- \rightarrow 2H_2O$	+1.23
$Pt^{2+}(aq) + 2e^- \rightarrow Pt(s)$	+1.18
$MnO_2(s) + 4H^+(aq) + e^- \rightarrow Mn^{3+} + 2H_2O$	+0.96
$NO_3^-(aq) + 4H^+(aq) + 3e^- \rightarrow NO(g) + 2H_2O$	+0.96
$Pd^{2+}(aq) + 2e^- \rightarrow Pd(s)$	+0.92
$Ag^+(aq) + e^- \rightarrow Ag(s)$	+0.80
$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$	+0.77
$Cu^+(aq) + e^- \rightarrow Cu(s)$	+0.53
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	+0.34
$BiO^+(aq) + 2H^+(aq) + 3e^- \rightarrow Bi(s) + H_2O$	+0.32
$Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}(aq)$	+0.15
$2H^+(aq) + 2e^- \rightarrow H_2(g)$	0 (by definition)
$Fe^{3+}(aq) + 3e^- \rightarrow Fe(s)$	–0.04
$Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$	–0.13
$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$	–0.14
$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$	–0.24
$Cd^{2+}(aq) + 2e^- \rightarrow Cd(s)$	–0.40
$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$	–0.44
$Cr^{3+}(aq) + 3e^- \rightarrow Cr(s)$	–0.74
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	–0.76
$2H_2O + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$	–0.83
$Cr^{2+}(aq) + 2e^- \rightarrow Cr(s)$	–0.89
$Al^{3+}(aq) + 3e^- \rightarrow Al(s)$	–1.68
$Sc^{3+}(aq) + 3e^- \rightarrow Sc(s)$	–2.09
$Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$	–2.36
$Na^+(aq) + e^- \rightarrow Na(s)$	–2.71
$Ca^{2+}(aq) + 2e^- \rightarrow Ca(s)$	–2.87
$Li^+(aq) + e^- \rightarrow Li(s)$	–3.04

CHEM1901 - CHEMISTRY 1A (ADVANCED)

CHEM1903 - CHEMISTRY 1A (SPECIAL STUDIES PROGRAM)

Useful formulas

Quantum Chemistry $E = h\nu = hc/\lambda$ $\lambda = h/mv$ $E = -Z^2E_R(1/n^2)$ $\Delta x\cdot\Delta(mv) \geq h/4\pi$ $q = 4\pi r^2 \times 5.67 \times 10^{-8} \times T^4$ $T\lambda = 2.898 \times 10^6$ K nm	**Electrochemistry** $\Delta G^\circ = -nFE^\circ$ *Moles of* e^- $= It/F$ $E = E^\circ - (RT/nF) \times \ln Q$ $E^\circ = (RT/nF) \times \ln K$ $E = E^\circ - \frac{0.0592}{n}\log Q$ (at 25 °C)
Acids and Bases $\mathrm{pH} = -\log[\mathrm{H}^+]$ $\mathrm{p}K_w = \mathrm{pH} + \mathrm{pOH} = 14.00$ $\mathrm{p}K_w = \mathrm{p}K_a + \mathrm{p}K_b = 14.00$ $\mathrm{pH} = \mathrm{p}K_a + \log\{[\mathrm{A}^-] / [\mathrm{HA}]\}$	**Gas Laws** $PV = nRT$ $(P + n^2a/V^2)(V - nb) = nRT$ $E_k = \frac{1}{2}mv^2$
Radioactivity $t_{1/2} = \ln 2/\lambda$ $A = \lambda N$ $\ln(N_0/N_t) = \lambda t$ $^{14}\mathrm{C}$ age = 8033 $\ln(A_0/A_t)$ years	**Kinetics** $t_{1/2} = \ln 2/k$ $k = Ae^{-Ea/RT}$ $\ln[\mathrm{A}] = \ln[\mathrm{A}]_0 - kt$ $\ln\frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$
Colligative Properties & Solutions $\Pi = cRT$ $P_{\mathrm{solution}} = X_{\mathrm{solvent}} \times P^\circ_{\mathrm{solvent}}$ $c = kp$ $\Delta T_f = K_f m$ $\Delta T_b = K_b m$	**Thermodynamics & Equilibrium** $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ $\Delta G = \Delta G^\circ + RT\ln Q$ $\Delta G^\circ = -RT\ln K$ $\Delta_{\mathrm{univ}}S^\circ = R\ln K$ $K_p = K_c\left(\frac{RT}{100}\right)^{\Delta n}$
Miscellaneous $A = -\log\frac{I}{I_0}$ $A = \varepsilon cl$ $E = -A\frac{e^2}{4\pi\varepsilon_0 r}N_A$	**Mathematics** If $ax^2 + bx + c = 0$, then $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$ $\ln x = 2.303\log x$ Area of circle = πr^2 Surface area of sphere = $4\pi r^2$

PERIODIC TABLE OF THE ELEMENTS

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 HYDROGEN **H** 1.008																	2 HELIUM **He** 4.003
3 LITHIUM **Li** 6.941	4 BERYLLIUM **Be** 9.012											5 BORON **B** 10.81	6 CARBON **C** 12.01	7 NITROGEN **N** 14.01	8 OXYGEN **O** 16.00	9 FLUORINE **F** 19.00	10 NEON **Ne** 20.18
11 SODIUM **Na** 22.99	12 MAGNESIUM **Mg** 24.31											13 ALUMINIUM **Al** 26.98	14 SILICON **Si** 28.09	15 PHOSPHORUS **P** 30.97	16 SULFUR **S** 32.07	17 CHLORINE **Cl** 35.45	18 ARGON **Ar** 39.95
19 POTASSIUM **K** 39.10	20 CALCIUM **Ca** 40.08	21 SCANDIUM **Sc** 44.96	22 TITANIUM **Ti** 47.88	23 VANADIUM **V** 50.94	24 CHROMIUM **Cr** 52.00	25 MANGANESE **Mn** 54.94	26 IRON **Fe** 55.85	27 COBALT **Co** 58.93	28 NICKEL **Ni** 58.69	29 COPPER **Cu** 63.55	30 ZINC **Zn** 65.39	31 GALLIUM **Ga** 69.72	32 GERMANIUM **Ge** 72.59	33 ARSENIC **As** 74.92	34 SELENIUM **Se** 78.96	35 BROMINE **Br** 79.90	36 KRYPTON **Kr** 83.80
37 RUBIDIUM **Rb** 85.47	38 STRONTIUM **Sr** 87.62	39 YTTRIUM **Y** 88.91	40 ZIRCONIUM **Zr** 91.22	41 NIOBIUM **Nb** 92.91	42 MOLYBDENUM **Mo** 95.94	43 TECHNETIUM **Tc** [98.91]	44 RUTHENIUM **Ru** 101.07	45 RHODIUM **Rh** 102.91	46 PALLADIUM **Pd** 106.4	47 SILVER **Ag** 107.87	48 CADMIUM **Cd** 112.40	49 INDIUM **In** 114.82	50 TIN **Sn** 118.69	51 ANTIMONY **Sb** 121.75	52 TELLURIUM **Te** 127.60	53 IODINE **I** 126.90	54 XENON **Xe** 131.30
55 CAESIUM **Cs** 132.91	56 BARIUM **Ba** 137.34	57-71	72 HAFNIUM **Hf** 178.49	73 TANTALUM **Ta** 180.95	74 TUNGSTEN **W** 183.85	75 RHENIUM **Re** 186.2	76 OSMIUM **Os** 190.2	77 IRIDIUM **Ir** 192.22	78 PLATINUM **Pt** 195.09	79 GOLD **Au** 196.97	80 MERCURY **Hg** 200.59	81 THALLIUM **Tl** 204.37	82 LEAD **Pb** 207.2	83 BISMUTH **Bi** 208.98	84 POLONIUM **Po** [210.0]	85 ASTATINE **At** [210.0]	86 RADON **Rn** [222.0]
87 FRANCIUM **Fr** [223.0]	88 RADIUM **Ra** [226.0]	89-103	104 RUTHERFORDIUM **Rf** [261]	105 DUBNIUM **Db** [262]	106 SEABORGIUM **Sg** [263]	107 BOHRIUM **Bh** [264]	108 HASSIUM **Hs** [265]	109 MEITNERIUM **Mt** [268]	110 DARMSTADTIUM **Ds** [281]	111 ROENTGENIUM **Rg** [272]	112 COPERNICIUM **Cn** [285]						

LANTHANOIDS	57 LANTHANUM **La** 138.91	58 CERIUM **Ce** 140.12	59 PRASEODYMIUM **Pr** 140.91	60 NEODYMIUM **Nd** 144.24	61 PROMETHIUM **Pm** [144.9]	62 SAMARIUM **Sm** 150.4	63 EUROPIUM **Eu** 151.96	64 GADOLINIUM **Gd** 157.25	65 TERBIUM **Tb** 158.93	66 DYSPROSIUM **Dy** 162.50	67 HOLMIUM **Ho** 164.93	68 ERBIUM **Er** 167.26	69 THULIUM **Tm** 168.93	70 YTTERBIUM **Yb** 173.04	71 LUTETIUM **Lu** 174.97
ACTINOIDS	89 ACTINIUM **Ac** [227.0]	90 THORIUM **Th** 232.04	91 PROTACTINIUM **Pa** [231.0]	92 URANIUM **U** 238.03	93 NEPTUNIUM **Np** [237.0]	94 PLUTONIUM **Pu** [239.1]	95 AMERICIUM **Am** [243.1]	96 CURIUM **Cm** [247.1]	97 BERKELLIUM **Bk** [247.1]	98 CALIFORNIUM **Cf** [252.1]	99 EINSTEINIUM **Es** [252.1]	100 FERMIUM **Fm** [257.1]	101 MENDELEVIUM **Md** [256.1]	102 NOBELIUM **No** [259.1]	103 LAWRENCIUM **Lr** [260.1]