#### **Topics in the June 2008 Exam Paper for CHEM1101**

Click on the links for resources on each topic.

#### 2008-J-2:

Nuclear and Radiation Chemistry

#### 2008-J-3:

• Band Theory - MO in Solids

#### 2008-J-4:

• Filling Energy Levels in Atoms Larger than Hydrogen

#### 2008-J-5:

• Wave Theory of Electrons and Resulting Atomic Energy Levels

#### 2008-J-6:

#### 2008-J-7:

- Lewis Structures
- VSEPR

#### 2008-J-8:

• Bonding - MO theory (larger molecules)

#### 2008-J-9:

• Chemical Equilibrium

#### 2008-J-10:

- Chemical Equilibrium
- Equilibrium and Thermochemistry in Industrial Processes

#### 2008-J-11:

- Polymers and the Macromolecular Consequences of Intermolecular Forces
- Thermochemistry
- First and Second Law of Thermodynamics

#### 2008-J-12:

- Thermochemistry
- First and Second Law of Thermodynamics

#### 2008-J-13:

- Thermochemistry
- First and Second Law of Thermodynamics

#### 2008-J-14:

- Electrochemistry
- Batteries and Corrosion
- Electrolytic Cells

2008-J-15:

• Electrolytic Cells

# The University of Sydney

#### **CONFIDENTIAL**

## CHEMISTRY 1A - CHEM1101

## **FIRST SEMESTER EXAMINATION**

#### **JUNE 2008**

#### **TIME ALLOWED: THREE HOURS**

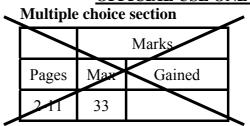
GIVE THE FOLLOWING INFORMATION IN BLOCK LETTERS

<b>FAMILY</b>	SID	
NAME	NUMBER	
OTHER	TABLE	
<b>NAMES</b>	NUMBER	

## **INSTRUCTIONS TO CANDIDATES**

- All questions are to be attempted. There are 24 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 •.
- Electronic calculators, including programmable calculators, may be used. Students are warned, however, 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 19, 23 and 28 are for rough working only.

## **OFFICIAL USE ONLY**



#### **Short answer section**

	Marks			
Page	Max	Gaine	d	Marker
12	5			
13	2			
14	4			
15	4			
16	4			
17	4			
18	6			
20	4			
21	5			
22	5			
24	6			
25	6			
26	6			
27	6			
Total	67			
Check	total			

CHEM1101 2008-J-2 June 2008 22/05(a)

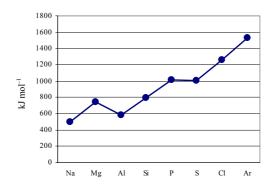
****	0555	Marks
Write two possible mechanisms for the ra	adioactive decay of <sup>33</sup> Fe to <sup>33</sup> Mn.	5
The activity of an isotopically pure 1 000	of sample of 55Fe is measured as	
The activity of an isotopically pure 1.000 $8.750 \times 10^{13}$ Bq. Calculate the half-life (The molar mass of <sup>55</sup> Fe is 54.94 g mol <sup>-1</sup>	in days) of <sup>55</sup> Fe.	
(The molar mass of <sup>55</sup> Fe is 54.94 g mol <sup>-1</sup>	.)	
	Answer:	
How many years will it take for the active to $1.000 \times 10^9$ Bq?	ity of this pure 1.000 g sample of <sup>55</sup> Fe to drop	)
<del>-</del>		
	Answer:	

Pure silicon is an insulator. Explain, with sketches of band structure diagrams, how 'doping' pure silicon with a small amount of phosphorus can turn it into an 'n-type' semiconductor.	Marks 2

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY

• The graph shows the first ionisation energies for third row elements of the periodic table.

Marks 4



Explain the general trend and both anomalies.

• Moseley discovered experimentally in 1913 that the atomic number, Z, of an element is inversely proportional to the square root of the wavelength,  $\lambda$ , of fluorescent X-rays emitted when an electron drops from the n = 2 to the n = 1 shell.

2008-J-5

Marks 4

i.e. 
$$\frac{1}{\sqrt{\lambda}} = kZ$$

Derive an expression for the constant of proportionality, k, for a hydrogen-like atom which would allow the value of k to be theoretically calculated.

CHEM1101 2008-J-6 June 2008 22/05(a)

•	Cadmium chloride and cadmium sulfate are both soluble in water. Cadmium carbonate, cadmium phosphate and cadmium hydroxide are all insoluble. Describe, using equations where appropriate, how to convert cadmium chloride into cadmium sulfate.	Marks 4

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY

• Modern plants, algae and cyanobacteria contain a class of pigments called chlorophyll. The structure of "chlorophyll a", which absorbs both red and blue light, is shown below.

Marks 4

Draw the full Lewis structure of the functional group shown in box "a".

What type of functional group is it?

Determine the local geometry of all other atoms bonded to each atom labelled on the structure above, and complete the table below.

Site	b	c	d	e
Geometry	tetrahedral			

• Carbon and nitrogen can combine to form a cyanide ion or a neutral free radical.

Marks 6

The molecular orbital energy level diagram provided shows the energies of the orbitals for the valence electrons in the free radical CN. Indicate on this diagram the ground state electronic configuration of CN using the arrow notation for electron spins.

<b>↑</b>	— σ*
	— π*
Energy	$\frac{-\sigma}{-\sigma}$ $\pi$
	— σ

How would you expect the magnetic properties of CN to differ from that of CN<sup>-</sup>?

How would adding an electron to CN to form CN<sup>-</sup> affect the strength of the bond between the two atoms? Explain your answer.

Why do we only need to consider the valence electrons when discussing the bonding of CN?

• Explain the difference between an equilibrium constant and a reaction quotient.

Marks 2

The following reactions have been demonstrated in mammalian liver at 37  $^{\circ}$ C and pH 7.5.

2

aspartate + citrulline  $\longrightarrow$  argininosuccinate + H<sub>2</sub>O  $K_{eq} = 13$ 

argininosuccinate  $\rightleftharpoons$  arginine + fumarate  $K_{eq} = 4.5$ 

fumarate +  $NH_4^+$   $\rightleftharpoons$  aspartate  $K_{eq} = 0.17$ 

Calculate the equilibrium constant at 37 °C and pH 7.5 for the following reaction.

arginine +  $H_2O$   $\rightleftharpoons$  citrulline +  $NH_4^+$ 

Answer:

• Methanol, CH<sub>3</sub>OH, is produced commercially by the catalysed reaction of carbon monoxide and hydrogen gas.  $K_p$  for this reaction at 600 K is  $1.13 \times 10^{-6}$ .

Marks 5

$$CO(g) + 2H_2(g)$$
  $\rightleftharpoons$   $CH_3OH(g)$ 

The reaction is exothermic, yet the equilibrium favours the reactants. Explain why this is the case.

The reaction vessel at 600 K is filled with 20.0 atm of CO(g) and 20.0 atm  $H_2(g)$ . What is the final pressure of  $CH_3OH(g)$  at equilibrium?

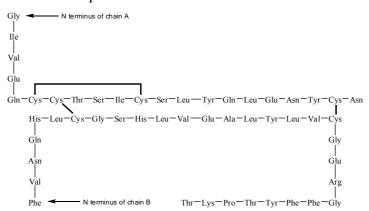
Answer:

Under what conditions of temperature and pressure do you think an industrial reactor would function to optimise the production of methanol? Explain.

Marks

2

• Insulin is an important hormone involved in the regulation of glucose availability in the body. It consists of two peptide chains, one consisting of 21 amino acids (the "A" chain) and one of 30 amino acids (the "B" chain). Below is a representation of insulin showing the amino acid sequence.



Define the terms *primary structure* and *secondary structure* in relation to proteins. In your definition, describe the atomic or molecular forces that are involved in the formation of the primary and secondary structure.

• The net amount of carbon dioxide fixed by photosynthesis on Earth has been estimated as  $5.5 \times 10^{16} \, \mathrm{g \ year}^{-1}$ . Calculate the energy stored by photosynthesis each year, assuming that all this carbon is converted into glucose,  $C_6H_{12}O_6$ .

 $\Delta_f \textit{H}^o \text{: } C_6 H_{12} O_6(s) \text{: } -1273 \text{ kJ mol}^{-1}, \ H_2 O(l) \text{: } -285.8 \text{ kJ mol}^{-1}, \ CO_2(g) \text{: } -393.5 \text{ kJ mol}^{-1}$ 

3

Answer:

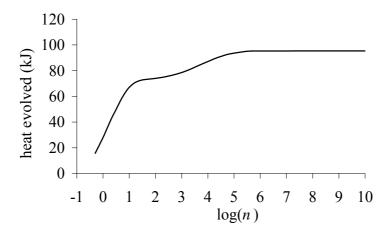
•	Sulfuric acid produced industrially must be diluted for many of its applications. This process is always carried out by adding the acid to water rather than by adding water to the acid. Use the data below to show that $\Delta_r H^0$ for the dilution of 50.0 mL of $H_2SO_4(l)$ to 1.00 L of $H_2SO_4(aq)$ is $-89$ kJ.	Marks 6
	$H_2SO_4(1)$ : $\Delta_f H^\circ = -814 \text{ kJ mol}^{-1}$ , density = 1.831 g mL <sup>-1</sup> , $C = 1.42 \text{ J g}^{-1} \text{ K}^{-1}$	
	H <sub>2</sub> SO <sub>4</sub> (aq): $\Delta_f H^{\circ} = -909 \text{ kJ mol}^{-1}$ , density = 1.060 g mL <sup>-1</sup> , $C = 3.50 \text{ J g}^{-1} \text{ K}^{-1}$	
	The dilution is carried out in a calorimeter. If the initial temperature of the system is 25.0 °C, what is the final temperature after dilution?	
Ì	Final tomporatura:	

Using the concept of heat capacity, explain why the dilution of sulfuric acid is carried out by adding acid to water rather than water to acid.

Marks 6

$$H_2SO_4(1)$$
:  $C = 1.42 \text{ J g}^{-1} \text{ K}^{-1}$ ,  $H_2O(1)$ :  $C = 4.18 \text{ J g}^{-1} \text{ K}^{-1}$ 

The figure below shows the heat evolved when one mole of  $H_2SO_4$  is mixed with n moles of  $H_2O$ . Explain the shape of curve.

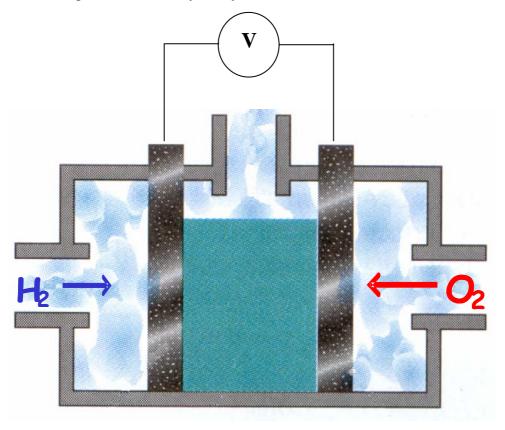


CHEM1101 2008-J-14 June 2008 22/05(a)

• Impure copper can be purified by electronelectrode and the purified copper as the anode in the electrolysis cell?	olysis, with the impure copper as one other. Is the impure copper the cathode or the	Mar 6
If a battery is used as the power source, connected to the impure copper or to the	<del>-</del>	
If electrolysis for 1.0 hour with a current calculate the oxidation number of the co	t of 5.2 A produces 5.9 g of pure copper, pper dissolved in the cell.	
	Oxidation number:	
	ion potentials, why a silver impurity in the silver metal, but a nickel impurity is found	
Explain what happens to an iron impurit	y in the Cu.	

• Hydrogen burns or explodes when it reacts with oxygen, but hydrogen and oxygen can be used to generate electricity safely in a fuel cell.

Marks 6



What reaction occurs at the H<sub>2</sub> electrode?

What reaction occurs at the O<sub>2</sub> electrode?

In which direction do the electrons flow?

What is conducted through the inert membrane from the hydrogen to the oxygen electrode?

What is the maximum voltage that this cell can generate under standard conditions?

How might this voltage be increased by changing the operating conditions?

#### **CHEM1101 - CHEMISTRY 1A**

#### **DATA SHEET**

#### Physical constants

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

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

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

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

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

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

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

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

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

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

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

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

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

#### Properties of matter

Volume of 1 mole of ideal gas at 1 atm and 25  $^{\circ}$ C = 24.5 L

Volume of 1 mole of ideal gas at 1 atm and  $0 \, ^{\circ}\text{C} = 22.4 \, \text{L}$ 

Density of water at 298 K = 0.997 g cm<sup>-3</sup>

#### Conversion factors

1  atm = 760  mmHg = 101.3  kPa	$1 \text{ Ci} = 3.70 \times 10^{10} \text{ Bq}$
0 °C = 273 K	$1 \text{ Hz} = 1 \text{ s}^{-1}$
$1 L = 10^{-3} m^3$	$1 \text{ tonne} = 10^3 \text{ kg}$
$1 \text{ Å} = 10^{-10} \text{ m}$	$1 \text{ W} = 1 \text{ J s}^{-1}$
$1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$	

#### Decimal fractions Decimal multiples Fraction Prefix Multiple Prefix Symbol Symbol $10^{-3}$ $10^{3}$ milli kilo k m $10^{-6}$ $10^{6}$ micro M mega μ $10^{-9}$ $10^{9}$ giga G nano n $10^{-12}$ pico p

## CHEM1101 - CHEMISTRY 1A

Standard Reduction Potentials,  $E^{\circ}$ 

Reaction	$E^{\circ}$ / $V$
$Co^{3+}(aq) + e^- \rightarrow Co^{2+}(aq)$	+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
$\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Cl}^-(\text{aq})$	+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
$\operatorname{Sn}^{4+}(\operatorname{aq}) + 2\operatorname{e}^{-} \to \operatorname{Sn}^{2+}(\operatorname{aq})$	+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
$Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$	-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

## CHEM1101 - CHEMISTRY 1A

## Useful formulas

031	Osejui jormuias			
Quantum Chemistry	Electrochemistry			
$E = hv = hc/\lambda$	$\Delta G^{\circ} = -nFE^{\circ}$			
$\lambda = h/mv$	$Moles\ of\ e^- = It/F$			
$E = -Z^2 E_{\rm R}(1/n^2)$	$E = E^{\circ} - (RT/nF) \times 2.303 \log Q$			
$\Delta x \cdot \Delta(mv) \ge h/4\pi$	$= E^{\circ} - (RT/nF) \times \ln Q$			
$q = 4\pi r^2 \times 5.67 \times 10^{-8} \times T^4$	$E^{\circ} = (RT/nF) \times 2.303 \log K$			
$4.5k_{\rm B}T = hc/\lambda$	$= (RT/nF) \times \ln K$			
$T = 2.898 \times 10^6 / \lambda (\text{nm})$	$E = E^{\circ} - \frac{0.0592}{n} \log Q \text{ (at 25 °C)}$			
Acids and Bases	Gas Laws			
$pK_{w} = pH + pOH = 14.00$	PV = nRT			
$pK_{\rm w} = pK_{\rm a} + pK_{\rm b} = 14.00$	$(P + n^2 a/V^2)(V - nb) = nRT$			
$pH = pK_a + \log\{[A^-] / [HA]\}$				
Colligative properties	Kinetics			
$\pi = cRT$	$t_{1/2} = \ln 2/k$			
$P_{\text{solution}} = X_{\text{solvent}} \times P_{\text{solvent}}^{\circ}$	$k = Ae^{-Ea/RT}$			
p = kc	$ ln[A] = ln[A]_{o} - kt $			
$\Delta T_{\rm f} = K_{\rm f} m$	$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$			
$\Delta T_{\rm b} = K_{\rm b} m$	$k_1 R T_1 T_2$			
Radioactivity	Thermodynamics & Equilibrium			
$t_{1/2} = \ln 2/\lambda$	$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ}$			
$A = \lambda N$	$\Delta G = \Delta G^{\circ} + RT \ln Q$			
$\ln(N_0/N_{\rm t}) = \lambda t$	$\Delta G^{\circ} = -RT \ln K$			
$^{14}$ C age = 8033 ln( $A_0/A_t$ ) years	$K_{\rm p} = K_{\rm c} \left( RT \right)^{\Delta n}$			
Miscellaneous	Mathematics			
$A = -\log \frac{I}{I_0}$	If $ax^2 + bx + c = 0$ , then $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$			
$A = \varepsilon c l$	$ \ln x = 2.303 \log x $			
$E = -A \frac{e^2}{4\pi\varepsilon_0 r} N_{\rm A}$				

### PERIODIC TABLE OF THE ELEMENTS

5 1 2 3 6 8 10 11 12 13 14 15 16 17 18 2 HYDROGEN HELIUM Η He 1.008 4.003 3 8 10 6 BERYLLIUM CARBON FLUORINE LITHIUM BORON NITROGEN OXYGEN Li Be В  $\mathbf{C}$ N 0  $\mathbf{F}$ Ne 14.01 6.941 9.012 10.81 12.01 19.00 20.18 16.00 13 14 15 11 12 16 17 18 MAGNESIUM ALUMINIUM CHLORINE SODIUM SILICON PHOSPHORUS SULFUR ARGON Na Al Si P S Mg Cl Ar 22.99 24.31 26.98 28.09 30.97 32.07 35.45 39.95 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 POTASSIUM SCANDIUM CHROMIUM COPPER CALCIUM TITANIUM VANADIUM MANGANESE IRON COBALT NICKEL GALLIUM GERMANIUM ARSENIC SELENIUM KRYPTON Ti  $\mathbf{V}$ K Ca Sc Fe Ni Kr Cr Mn Co Cu Zn Ga Ge As Se Br 39.10 40.08 44.96 47.88 50.94 52.00 54.94 55.85 58.93 58.69 63.55 65.39 69.72 72.59 74.92 78.96 79.90 83.80 37 38 39 40 41 42 43 44 45 47 48 49 50 51 52 53 54 46 MOLYBDENUM TECHNETIUM CADMIUM RUBIDIUM STRONTIUM YTTRIUM ZIRCONIUM NIOBIUM RUTHENIUM RHODIUM PALLADIUM SILVER INDIUM ANTIMONY TELLURIUM IODINE XENON Rb  $\mathbf{Y}$ Tc Sr Zr Nb Mo Ru Rh Pd Ag Cd In Sn Sb Te Ι Xe [98.91] 85.47 87.62 88.91 91.22 92.91 95.94 101.07 102.91 106.4 107.87 112.40 114.82 118.69 121.75 127.60 126.90 131.30 55 56 57-71 72 73 77 78 79 81 82 83 84 85 86 74 75 76 80 CAESIUM BARIUM HAFNIUM TANTALUM TUNGSTEN RHENIUM OSMIUM IRIDIUM PLATINUM GOLD MERCURY THALLIUM LEAD BISMUTH POLONIUM ASTATINE RADON Tl Pb Hf W Pt Cs Ba Ta Re Os Ir Au Hg Bi Po At Rn 132.91 207.2 208.98 [210.0] 137.34 178.49 180.95 183.85 186.2 190.2 192.22 195.09 196.97 200.59 204.37 [210.0] [222.0] 87 88 89-103 104 105 106 107 108 109 110 111 FRANCIUM RADIUM DUBNIUM SEABORGIUM BOHRIUM HASSIUM MEITNERIUM ARMSTADTIUM OENTGENIUM  $\mathbf{Fr}$ Ra Rf Db Sg Bh Hs Mt Ds Rg [223.0] [226.0] [261] [262] [262] [265] [266] [271] [272] [266]

LANTHANIDES

ACTINIDES

3	57 Lanthanum <b>La</b> 138.91	58 CERIUM Ce 140.12	59 PRASEODYMIUM <b>Pr</b> 140.91	60 NEODYMIUM <b>Nd</b> 144.24	61 PROMETHIUM <b>Pm</b> [144.9]	62 Samarium <b>Sm</b> 150.4	63 Europium <b>Eu</b> 151.96	64 GADOLINIUM <b>Gd</b> 157.25	65 TERBIUM <b>Tb</b> 158.93	66 Dysprosium <b>Dy</b> 162.50	67 ногмим <b>Но</b> 164.93	68 Er 167.26	69 THULIUM Tm 168.93	70 <b>YTTERBIUM Yb</b> 173.04	71 Lu Lu 174.97
	89 Actinium <b>Ac</b> [227.0]	90 THORIUM <b>Th</b> 232.04	91 PROTACTINIUM <b>Pa</b> [231.0]	92 URANIUM U 238.03	93 NEPTUNIUM <b>Np</b> [237.0]	94 PLUTONIUM <b>Pu</b> [239.1]	95 AMERICIUM <b>Am</b> [243.1]	96 curium <b>Cm</b> [247.1]	97 Berkellium <b>Bk</b> [247.1]	98 CALIFORNIUM  Cf [252.1]	99 EINSTEINIUM ES [252.1]	100 FERMIUM <b>Fm</b> [257.1]	101 MENDELEVIUM <b>Md</b> [256.1]	102 Nobelium <b>No</b> [259.1]	103 Lawrencium <b>Lr</b> [260.1]