2020 Fall Semester Mid-term Examination
For General Chemistry I

Date: Oct 21 (Wed),   Time Limit: 19:00 ~ 22:00

NOTICE

- If you have a printer, print the papers and write the answers in the space of each question. If not, prepare several A4-size papers to write only question # and the answers on it in the following example. And for clarity, marking your answer is recommended. Please, print your Student ID in the upper right corner of every page for both of them. (***Handwriting only is acceptable*** and typing is not.)

  Example:

Professor Name	Class	Student I.D. Number	Name

  #1. (a)………

  (b)……..

- If you have any questions during the period, please contact the TA of your class using the Zoom chat channel to "Everyone" (the only possible choice). Proctors will make any announcements relevant to all students *via* audio.

- While still in the video conference, submit your file to [Midterm Examination], an assignment on Turnitin of your class. ***Do not leave the video conference*** until your TA is confirmed and tells you that it is fine to leave.

** This paper consists of 11 sheets with 10 problems (page 10 - 11: Equation, constants & periodic table). Please check all page numbers before taking the exam. Please write down the unit of your answer when applicable. You will get 30% deduction for a value that is missing its unit.

NOTICE: SCHEDULES on RETURN and CLAIM of the MARKED EXAM PAPER.
(채점 답안지 분배 및 이의신청 일정)

1. Period, Location, and Procedure

1) Return and Claim Period: Oct **26** ***(Mon 12:00~24:00)***
2) ***Location: Each class of Turnitin site (online)***
3) Procedure: If you have any claims on it, email them (Question# and reasons) to your TA.

(The claim is permitted only during the designated claim period. Keep that in mind! A solution file with answers for the examination will be uploaded on the web.)

2. Final Confirmation

1) Period: Oct **29-30** (***Thu – Fri***)
2) Procedure: During this period, you can check final score of the examination *on the website* again.

(No additional corrections. If no change in your score after reasoning, the claims were not accepted.)

***** For further information, please visit General Chemistry website at www.gencheminkaist.pe.kr***

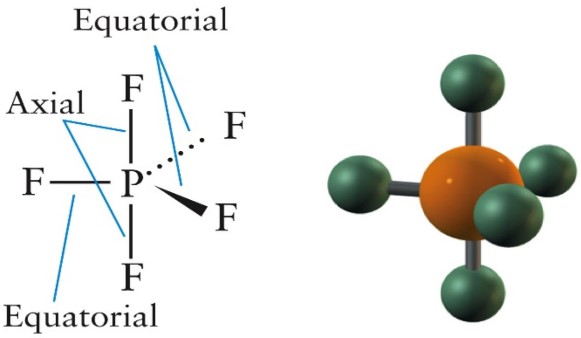
1. (total 10 pts)

For phosphorus pentafluoride, PF_5, answer the following questions.

(a) Draw and name the shape of the molecule. (4 pts)

(Answer)

Steric number = 5



Trigonal bipyramid

Molecular structure ***+2 pts***
(If three-dimensional indication is missing, only ***+1 pt*** available)
Name of the structure: Trigonal bipyramid ***+2 pts***

(b) Do the equatorial P-F and axial P-F have the same length or different lengths? Explain the reason. (6 pts)

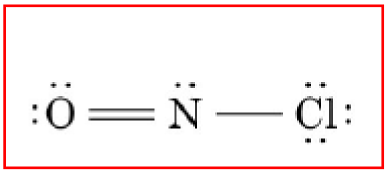
(Answer)

They have different bond lengths. ***+2 pts***
(Axial bond length (1.577 Å) > Equatorial bond length (1.534 Å))
Axial Fs experience three 90° repulsions, while equatorial Fs have two 90° repulsions. ***+2 pts***
Hence the axial Fs feel higher repulsion and the bond lengths become longer. ***+2 pts***

2. (total 10 pts, each 2 pts)

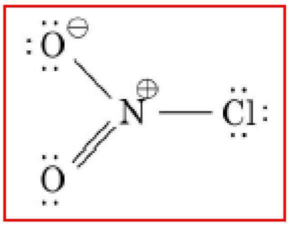
Draw Lewis diagrams and write down the predicted geometries of the following molecules, and write whether they are polar or nonpolar.

(a) ONCl



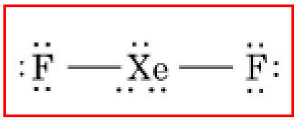
,bent, polar

(b) O_2NCl



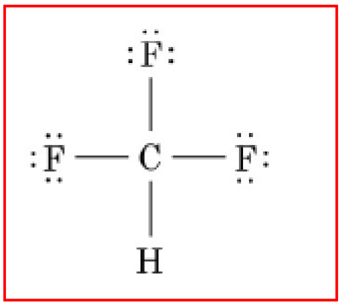
Trigonal Planar, Polar (You should express the formal charge)

(c) XeF_2



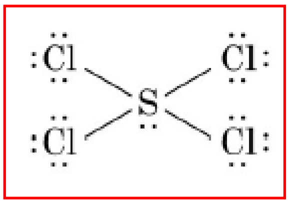
Linear, Non-polar

(d) CHF_3



Tetrahedral, Polar

(e) SCl_4



Seesaw, polar

3. (total 10 pts, each 2.5 pts)

For the given atomic orbital, answer the following questions below

$$R_{nl} = \frac{4}{81\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2}(6\sigma - \sigma^2)\exp\left(-\frac{\sigma}{3}\right), \qquad Y_{\text{lm}} = \left(\frac{3}{4\pi}\right)^{1/2}\sin\theta\,\sin\phi$$

(a) From the radial part of the wavefunction, what is the number of radial nodes? Express the number of radial nodes with n and l.

(b) From the angular part of the wavefunction, what is the angular nodal plane?

(c) From 1 and 2, find the principle quantum number n and the angular momentum quantum number l.

(d) Using the process of 1–3), find the n and l for the below orbital, and give the name of this orbital.

$$R_{nl} = \frac{4}{81\sqrt{30}}\left(\frac{Z}{a_0}\right)^{3/2}\sigma^2\exp\left(-\frac{\sigma}{3}\right), \qquad Y_{\text{lm}} = \left(\frac{15}{4\pi}\right)^{1/2}\sin\theta\cos\theta\sin\phi$$

Answer

(a)

$$R_{3p} = \frac{4}{81\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2}(6\sigma - \sigma^2)\exp(-\sigma/3)$$

The wavefunction becomes 0 when σ is 0 or 6. So, the number of radial nodes is 1.

$1 = \text{n} - l - 1$

(b) There exists a radial node where $\phi = \pi$. This is the xz plane.

(c) Since there are l angular nodes for an orbital (n, l, m), l = 1 in this case.

Using the equation in 1), $1 = n - 1 - 1$, so n = 3

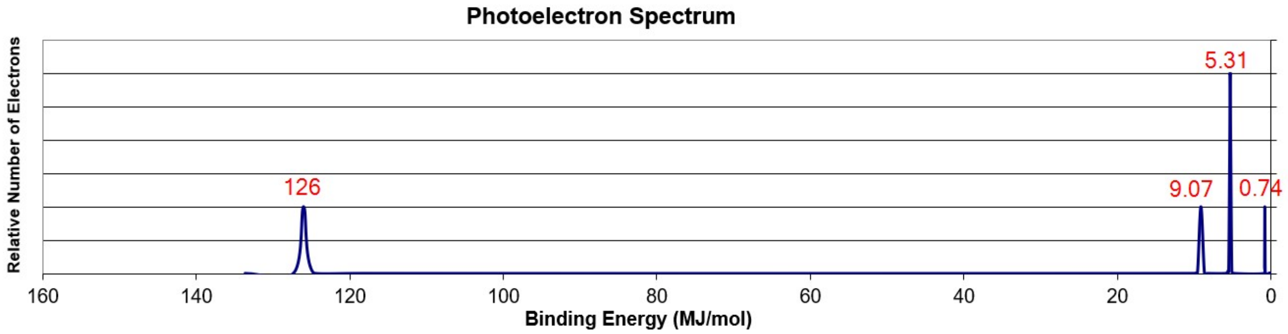
(d) There is no radial node. So, $0 = n - l - 1$

From the angular wavefunction, there are two nodal planes when $\theta = \frac{\pi}{2},\ \phi = \pi.$

So, l = 2, and n = 3. This is the 3d orbital.

4. (total 10 pts)

Using the photoelectron spectrum below, answer the following questions.



(a) (2 pts) What is the electron configuration of the element shown above?

(Answer)

$1s^2 2s^2 2p^6 3s^2$

(b) (2 pts) What element is illustrated?

(Answer)

Mg (magnesium)

(c) (6 pts) What is the wavelength required, in m, to remove a valence electron from the element shown above?

(Answer)

$$\frac{0.74MJ}{mol} \times \frac{10^6 J}{MJ} \times \frac{mol}{6.022 \times 10^{23}} = 1.23 \times 10^{-18} J$$

$$E = \frac{hc}{\lambda} = 1.23 \times 10^{-18} J \cdots \boldsymbol{2pt}$$

$$\lambda = \frac{hc}{E} = \frac{(6.626 \times 10^{-34} J \cdot s)(2.998 \times 10^8 m \cdot s^{-1})}{1.23 \times 10^{-18} J} = 1.62 \times 10^{-7} m$$

5. (total 10 pts)

(a) (5 pts) Write simple valence bond wave functions for the bonds in H_2O.

(b) (5 pts) What geometry does the VB model predict for H_2O? Justify your answer.

Answer

(a) The simple VB model predicts that O (valence electron configuration $2s^2 2p_x^1 2p_y^1 2p_z^2$) forms single bonds with each of the two H atoms. These atoms are designated H_1 and H_2 in the following valence-bond wave functions, which come from overlap of the $2p_x$ and $2p_y$ orbitals on the O with the respective 1s orbitals on the H's

$$\mathrm{O-H_1}: \ \psi_\sigma^{bond}(1,2;R_{\mathrm{OH_1}}) = c_1\left[1s^{\mathrm{H_1}}(1)2p_x^{\mathrm{O}}(2)\right] + c_2[1s^{\mathrm{H_1}}(2)2p_x^{\mathrm{O}}(1)]$$

$$\mathrm{O-H_2}: \ \psi_\sigma^{bond}(1,2;R_{\mathrm{OH_2}}) = c_1\left[1s^{\mathrm{H_2}}(1)2p_y^{\mathrm{O}}(2)\right] + c_2[1s^{\mathrm{H_2}}(2)2p_y^{\mathrm{O}}(1)]$$

(b) The model predicts (incorrectly) that the H—O—H angle equals 90°.

6. (total 10 pts)

(a) (4 pts) Predict the ground electronic state of the He_2^{2+} ion.

(b) (3 pts) What is the bond order?

(c) (3 pts) Will it be stable in the ground state? Justify your answer.

Answer

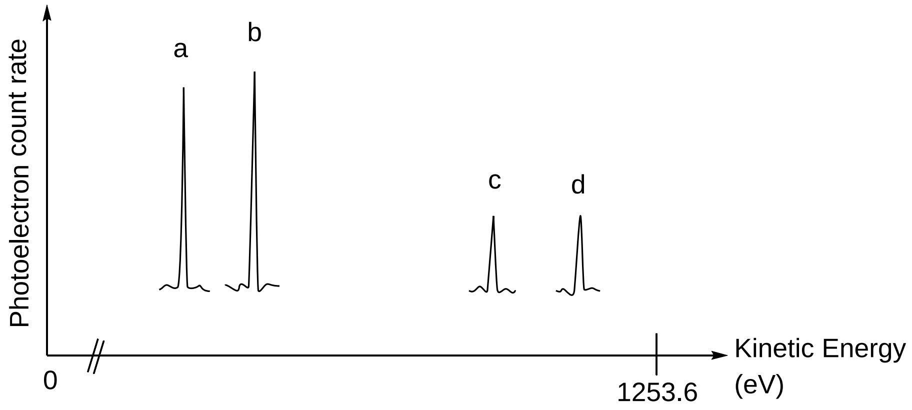
(a) The ground state electron configuration of the He_2^{2+} ion is $(\sigma_{1s})^2$.

(b) bond order: one.

(c) This configuration is stable in its ground state, because its bond order is nonzero..

7. (total 10 pts, each 2.5 pts)

The following figure shows the data obtained with photoelectron spectroscopy for Ne and Na with X-rays with λ = 9.890 x 10^{-10} m. Assign the peaks a–d with the 1^{st}, 2^{nd} ionization energy of each atom.



a :

b :

c :

d :

Answer

a: 2^{nd} ionization energy of Na.

b: 2^{nd} ionization energy of Ne

c: 1^{st} ionization energy of Ne

d: 1^{st} ionization energy of Na

8. (total 10 pts)

(a) Name the types of attractive forces that will contribute to the interactions among atoms, molecules, or ions in the following substances. Indicate the one(s) you expect to predominate. (each 2 pts)

(i) Ne

(ii) ClF

(iii) $BaCl_2$

(b) (4 pts) Predict whether an atom of argon will be most strongly attracted to another atom of argon, an atom of neon, or an atom of krypton.

Answer

(a) (i) dispersion forces (ii) dipole-dipole forces (predominant) and dispersion forces (iii) ion-ion forces (predominant) and dispersion forces

(b) An atom of argon should be most strongly attracted by an atom of krypton. The krypton atom has more electrons and is more polarizable than one of argon and the strength of dispersion forces depends on the polarizability of the interacting species.

9. (total 10 pts)

A sample of an oxide of osmium (1.509g) is gaseous at 200.0℃ / 0.980 atm pressure, and occupies 235mL under these conditions. Assuming the ideal gas behavior, determine the molecular formula of the oxide. [Molar masses (g mol^{-1}): Os = 190.2; O = 16.00. R = 0.08206 L atm K^{-1} mol^{-1}. Take 0℃ to be 273K]. Please show your work (partial points).

Answer

Since the gas has ideal behavior,

PV = nRT, where n = m/M_r (M_r is molar mass)

n = (0.980 atm)(0.235 L)/(0.0802 L atm/K mol)(473 K) = 0.00590 mol ----- **(3 pts)**

Hence M_r = (1.509 g)/0.00590 mol) = 254 g mol^{-1} --------- **(3 pts)**

If the molecular formula of the oxide is OsOx, then the molar mass is

192.0 g mol^{-1} + x(16.00 g mol^{-1}) = 254 g mol^{-1}

x = 3.99 ~ 4

Molecular formula is OsO4 (4 points)

10. (total 10 pts, each 2.5 pts)

The following formula is the van der Waals equation of gaseous state.

$$\left(P + a\frac{n^2}{V^2}\right)(V - nb) = nRT$$

(a) How is the compressibility factor *z* calculated in this condition?

(b) What is the dimension (unit) for *a* and *b*? (Use atm as a unit of pressure.)

(c) What is the meaning behind these constants?

(d) Compare the constants *a* and *b* of gaseous ammonia (NH_3) and hydrogen (H_2).

Answer

(a) $z = \frac{PV}{nRT} = \frac{V}{V-nb} - \frac{a}{RT}\frac{n}{V} = \frac{1}{1-bn/V} - \frac{a}{RT}\frac{n}{V}$

(b) a : atm L^2 mol^{-2}

b : L mol^{-1}

(c) *a* stands for the attractive force, while b stands for repulsive forces (the volume excluded by 1 mol of molecules)

(d) Comparing the gaseous ammonia (NH_3) and hydrogen (H_2), the ***a*** value for **ammonia** is more than 10 times larger than for **hydrogen**. However, the value for ***b*** for each is very similar.

(Full point for both of a and b, +1pt for only in number)

Physical Constants

Avogadro's number	$N_A = 6.02214179 \times 10^{23}$ mol^{-1}
Bohr radius	$a_0 = 0.52917720859$ Å $= 5.2917720859 \times 10^{-11}$ m
Boltzmann's constant	$K_B = 1.3806504 \times 10^{-23}$ J K^{-1}
Electronic charge	$e = 1.602176487 \times 10^{-19}$ C
Faraday constant	$F = 96485.3399$ C mol^{-1}
Masses of fundamental particles:	
Electron	$m_e = 9.10938215 \times 10^{-31}$ kg
Proton	$m_P = 1.672621637 \times 10^{-27}$ kg
Neutron	$m_n = 1.674927211 \times 10^{-27}$ kg
Permittivity of vacuum	$\varepsilon_o = 8.854187817 \times 10^{-12}$ C^{-2} J^{-1} m^{-1}
Planck's constant	$h = 6.62606896 \times 10^{-34}$ J s
Ratio of proton mass to electron mass	$m_P / m_e = 1836.15267247$
Speed of light in a vacuum	c = 2.99792458×10^{8} m s^{-1} (exactly)
Standard acceleration of terrestrial gravity	$g = 9.80665$ m s^{-2} (exactly)
Universal gas constant	$R = 8.314472$ J mol^{-1} K^{-1} $= 0.0820574$ L atm mol^{-1} K^{-1}

Values are taken from the 2006 CODATA recommended values,
as listed by the National Institute of Standards and Technology.

Conversion factors

Ångström	1 Å= 10^{-10} m
Atomic mass unit	1 u = $1.660538782 \times 10^{-27}$ kg
	1 u = $1.492417830 \times 10^{-10}$ J = 931.494028 MeV (energy equivalent form $E = mc^2$)
Calorie	1 cal = 4.184 J (exactly)
Electron volt	1 eV = 1.602177×10^{-19} J = 96.485335 kJ mol^{-1}
Foot	1 ft = 12 in = 0.3048 m (exactly)
Gallon (U. S.)	1 gallon = 4 quarts = 3.785412 L (exactly)
Liter	1 L = 10^{-3} m^{-3} = 10^{3} cm^{3} (exactly)
Liter-atmosphere	1 L atm = 101.325 J (exactly)
Metric ton	1 t = 1000 kg (exactly)
Pound	1 lb = 16 oz = 0.4539237 kg (exactly)
Rydberg	1 Ry = $2.17987197 \times 10^{-18}$J = 1312.7136 kJ mol^{-1} = 13.60569193 eV
Standard atmosphere	1 atm = 1.01325×10^{5} Pa = 1.01325×10^{5} kg m^{-1} s^{-2} (exactly)
Torr	1 torr = 133.3224 Pa

PERIODIC TABLE OF THE ELEMENTS

http://www.ktf-split.hr/periodni/en/

GROUP NUMBERS IUPAC RECOMMENDATION (1985) — 13; GROUP NUMBERS CHEMICAL ABSTRACT SERVICE (1986) — IIIA

ATOMIC NUMBER — 5; RELATIVE ATOMIC MASS (1) — 10.811; SYMBOL — B; ELEMENT NAME — BORON

PERIOD	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8	9 VIIIB	10	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1	1 1.0079 **H** HYDROGEN																	2 4.0026 **He** HELIUM
2	3 6.941 **Li** LITHIUM	4 9.0122 **Be** BERYLLIUM											5 10.811 **B** BORON	6 12.011 **C** CARBON	7 14.007 **N** NITROGEN	8 15.999 **O** OXYGEN	9 18.998 **F** FLUORINE	10 20.180 **Ne** NEON
3	11 22.990 **Na** SODIUM	12 24.305 **Mg** MAGNESIUM											13 26.982 **Al** ALUMINIUM	14 28.086 **Si** SILICON	15 30.974 **P** PHOSPHORUS	16 32.065 **S** SULPHUR	17 35.453 **Cl** CHLORINE	18 39.948 **Ar** ARGON
4	19 39.098 **K** POTASSIUM	20 40.078 **Ca** CALCIUM	21 44.956 **Sc** SCANDIUM	22 47.867 **Ti** TITANIUM	23 50.942 **V** VANADIUM	24 51.996 **Cr** CHROMIUM	25 54.938 **Mn** MANGANESE	26 55.845 **Fe** IRON	27 58.933 **Co** COBALT	28 58.693 **Ni** NICKEL	29 63.546 **Cu** COPPER	30 65.39 **Zn** ZINC	31 69.723 **Ga** GALLIUM	32 72.64 **Ge** GERMANIUM	33 74.922 **As** ARSENIC	34 78.96 **Se** SELENIUM	35 79.904 **Br** BROMINE	36 83.80 **Kr** KRYPTON
5	37 85.468 **Rb** RUBIDIUM	38 87.62 **Sr** STRONTIUM	39 88.906 **Y** YTTRIUM	40 91.224 **Zr** ZIRCONIUM	41 92.906 **Nb** NIOBIUM	42 95.94 **Mo** MOLYBDENUM	43 (98) **Tc** TECHNETIUM	44 101.07 **Ru** RUTHENIUM	45 102.91 **Rh** RHODIUM	46 106.42 **Pd** PALLADIUM	47 107.87 **Ag** SILVER	48 112.41 **Cd** CADMIUM	49 114.82 **In** INDIUM	50 118.71 **Sn** TIN	51 121.76 **Sb** ANTIMONY	52 127.60 **Te** TELLURIUM	53 126.90 **I** IODINE	54 131.29 **Xe** XENON
6	55 132.91 **Cs** CAESIUM	56 137.33 **Ba** BARIUM	57-71 **La-Lu** Lanthanide	72 178.49 **Hf** HAFNIUM	73 180.95 **Ta** TANTALUM	74 183.84 **W** TUNGSTEN	75 186.21 **Re** RHENIUM	76 190.23 **Os** OSMIUM	77 192.22 **Ir** IRIDIUM	78 195.08 **Pt** PLATINUM	79 196.97 **Au** GOLD	80 200.59 **Hg** MERCURY	81 204.38 **Tl** THALLIUM	82 207.2 **Pb** LEAD	83 208.98 **Bi** BISMUTH	84 (209) **Po** POLONIUM	85 (210) **At** ASTATINE	86 (222) **Rn** RADON
7	87 (223) **Fr** FRANCIUM	88 (226) **Ra** RADIUM	89-103 **Ac-Lr** Actinide	104 (261) **Rf** RUTHERFORDIUM	105 (262) **Db** DUBNIUM	106 (266) **Sg** SEABORGIUM	107 (264) **Bh** BOHRIUM	108 (277) **Hs** HASSIUM	109 (268) **Mt** MEITNERIUM	110 (281) **Uun** UNUNNILIUM	111 (272) **Uuu** UNUNUNIUM	112 (285) **Uub** UNUNBIUM		114 (289) **Uuq** UNUNQUADIUM				

LANTHANIDE

6	57 138.91 **La** LANTHANUM	58 140.12 **Ce** CERIUM	59 140.91 **Pr** PRASEODYMIUM	60 144.24 **Nd** NEODYMIUM	61 (145) **Pm** PROMETHIUM	62 150.36 **Sm** SAMARIUM	63 151.96 **Eu** EUROPIUM	64 157.25 **Gd** GADOLINIUM	65 158.93 **Tb** TERBIUM	66 162.50 **Dy** DYSPROSIUM	67 164.93 **Ho** HOLMIUM	68 167.26 **Er** ERBIUM	69 168.93 **Tm** THULIUM	70 173.04 **Yb** YTTERBIUM	71 174.97 **Lu** LUTETIUM

ACTINIDE

7	89 (227) **Ac** ACTINIUM	90 232.04 **Th** THORIUM	91 231.04 **Pa** PROTACTINIUM	92 238.03 **U** URANIUM	93 (237) **Np** NEPTUNIUM	94 (244) **Pu** PLUTONIUM	95 (243) **Am** AMERICIUM	96 (247) **Cm** CURIUM	97 (247) **Bk** BERKELIUM	98 (251) **Cf** CALIFORNIUM	99 (252) **Es** EINSTEINIUM	100 (257) **Fm** FERMIUM	101 (258) **Md** MENDELEVIUM	102 (259) **No** NOBELIUM	103 (262) **Lr** LAWRENCIUM

(1) Pure Appl. Chem., 73, No. 4, 667-683 (2001)
Relative atomic mass is shown with five significant figures. For elements have no stable nuclides, the value enclosed in brackets indicates the mass number of the longest-lived isotope of the element.
However three such elements (Th, Pa, and U) do have a characteristic terrestrial isotopic composition, and for these an atomic weight is tabulated.

Editor: Aditya Vardhan (adivar@nettlinx.com)

2020 Fall Semester Final Examination
For General Chemistry I

Date: Dec 16 (Wed), Time Limit: 19:00 ~ 22:00

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  Example:

Professor Name	Class	Student I.D. Number	Name

  #1. (a)………

  (b)……..

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(채점 답안지 분배 및 이의신청 일정)

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(No additional corrections. If no change in your score after reasoning, the claims were not accepted.)

***** For further information, please visit General Chemistry website at www.gencheminkaist.pe.kr***

1. (total 12 pts)

The following is a redox reaction commonly used for titration.

$$\mathrm{MnO_4^-}(aq) + \boldsymbol{a}\ \mathrm{Fe^{2+}}(aq) + \boldsymbol{b}\ \mathrm{H^+}(aq) \rightarrow \mathrm{Mn^{2+}}(aq) + \boldsymbol{c}\ \mathrm{Fe^{3+}}(aq) + \boldsymbol{d}\ \mathrm{A}\ (l)$$

(a) (4 pts) Find the values for ***a, b, c, d***, and the unknown chemical species A.

(b) (4 pts) 37.2 ml of 0.13 M $KMnO_4$ solution was used to titrate a sample of Fe^{2+}. The final volume after titration is 52.3 ml. What was the initial concentration of Fe^{2+} in the original solution?

(c) (4 pts) Potassium manganate can also be used for the titration of calcium ion. Suppose a 50 ml of 0.1 M $KMnO_4$ solution was used in the indirect titration of 5 ml of Ca^{2+} solution. What was the initial concentration of Ca^{2+} in the original solution? Do not need to specify ***e, f, g, h.***

$$\mathrm{Ca^{2+}}(aq) + \mathrm{C_2O_4^{2-}}(aq) \rightarrow \mathrm{CaC_2O_4}(s)$$

$$\mathrm{CaC_2O_4}(s) + 2\mathrm{H^+}(aq) \rightarrow \mathrm{Ca^{2+}}(aq) + \mathrm{H_2C_2O_4}(aq)$$

$$2\ \mathrm{MnO_4^-}(aq) + \boldsymbol{e}\ \mathrm{H_2C_2O_4}(aq) + \boldsymbol{f}\ \mathrm{H_3O^+}(aq) \rightarrow 2\ \mathrm{Mn^{2+}}(aq) + \boldsymbol{g}\ \mathrm{CO_2}(g) + \boldsymbol{h}\ \mathrm{H_2O}(l)$$

Answer

(a)

$$\mathrm{MnO_4^-}(aq) + 5\mathrm{Fe^{2+}}(aq) + 8\mathrm{H^+}(aq) \rightarrow \mathrm{Mn^{2+}}(aq) + 5\mathrm{Fe^{3+}}(aq) + 4\mathrm{H_2O}(l)$$

a = 5 / ***b*** = 8 / ***c*** = 5 / ***d*** = 4 / A = H_2O ***- Total 4 pts, 1 point for each value***

(b) MnO_4^- and Fe^2+ reacts in a 1:5 ratio. ***+1 point***

Thus,

37.2 ml * 0.13 M * 5= (52.3 – 37.2) ml * $[Fe^{2+}]_0$

$[Fe^{2+}]_0$ = 1.6 M ***- Full points for correct answer***

(c)

$$2\ \mathrm{MnO_4^-}(aq) + 5\ \mathrm{H_2C_2O_4}(aq) + 6\mathrm{H_3O^+}(aq) \rightarrow 2\ \mathrm{Mn^{2+}}(aq) + 10\ \mathrm{CO_2}(g) + 14\mathrm{H_2O}(l)$$

From the above equation, the molar reaction ratio between MnO_4^- and Ca^{2+} is 2:5. Thus, since 50 ml of 0.1M $KMnO_4$ solution contains 5 mmol of MnO_4^-, $[Ca^{2+}]$ * 5 ml = 5 mmol * (5/2) = 12.5 mmol. So, the $[Ca^2$+] = 2.5 M. ***- Full points for correct answer***

2. (total 10 pts)

The vapor pressure of pure liquid CS_2 is 0.3914 atm at 20°C. When 40.0g of rhombic sulfur is dissolved in 1.00kg of CS_2, the vapor pressure of CS_2 decreases to 0.3868 atm. Determine the molecular formula for the sulfur molecules dissolved in CS_2 and rationalize your answer.

Answer

$\Delta P = 0.3868 - 0.3914 = -0.0046$ atm.

Mole fraction of the sulfur present in the sulfur-CS_2 system, $X_{sulfur} = -\frac{\Delta P}{P°_{CS2}} = -(-0.0046\text{atm})/(0.3914\text{ atm}) = 0.0117$ ***+2 point***

1.00kg of CS_2 = 13.13 mol of CS_2, ***+2 point***

$X_{sulfur} = 0.0117 = n_{sulfur}/(n_{sulfur} + n_{CS2}) = n_{sulfur}/(n_{sulfur} + 13.13\text{ mol})$

$n_{sulfur} = 0.155$ mol. → 40.0g of sulfur ***+3 point***

molar mass = 40.0g/0.155mol = 257$gmol^{-1}$. Which is 8 times of 32$gmol^{-1}$(the molar mass of S).

Molecular formula = S_8 ***+3 point***

3. (total 8 pts, each 4 pts)

One mole of an ideal monatomic gas initially at 300K and a pressure of 15.0 atm expands to a final pressure of 1.00 atm. The expansion can occur via any one of three different paths: a) isothermal and reversible, b) isothermal and irreversible, c) adiabatic and reversible. In irreversible process, the expansion occurs against an external pressure of 1.00 atm. For the below cases, calculate the values of q, w, ΔU and ΔH.

(a) (1 pt for each quantity) isothermal and reversible

(b) (1 pt for each quantity) isothermal and irreversible.

Answer

(a) When an ideal gas undergoes an isothermal process, $\Delta U=0$ and $\Delta H=0$.

$w = -nRT\ln (P_1/P_2) = -$ (1mol) (8.314 $JK^{-1}mol^{-1}$)(300K) ln (15.0 atm/1.00atm) $= -6.75 \times 10^3$J.

$q = \Delta U - w = -w = 6.75 \times 10^3$J.

(b) for isothermal process, $\Delta U=0$ and $\Delta H=0$. $W = -P_{ex}(V_2 - V_1)$

V_1 and V_2 determined using ideal gas law:

$V_1 = nRT/P_1$ = [(1 mol)(0.08206$LatmK^{-1}mol^{-1}$)(300K)]/15.0 atm = 1.641L

$V_2 = nRT/P_2$ = [(1 mol)(0.08206$LatmK^{-1}mol^{-1}$)(300K)]/1.0 atm = 24.62L

W = -(1.00atm) (24.62L – 1.641L) (101.3J/1L atm) $= -2.33 \times 10^3$J

$q = \Delta U - w = -w = 2.33 \times 10^3$J

4. (total 10 pts)

Air is contained in an insulated, rigid volume at 20℃ and 2 atm. A paddle wheel, inserted in the volume, does 720 kJ of work on the air. If the volume is 2 m^3, calculate the entropy increase assuming a constant specific heat (0.717 J g^{-1} K^{-1}) and ideal-gas behavior. Rationalize your answer.

(Answer)

Mass of air

$$m = \frac{MPV}{RT} = \frac{(28.8\ g\ mol^{-1})(2\ atm)(2000\ L)}{(0.082\ L\ atm\ mol^{-1}\ K^{-1})(293\ K)} = 4780\ g$$ ***+3 point***

Internal energy $\Delta U = q + w = mc_s\Delta T$

$$720\ kJ = (4780\ g)\ (0.717\ J\ g^{-1}\ K^{-1})\ ((T_2 - 293)\ K) \quad \therefore T_2 = 503\ K$$ ***+3 point***

Entropy change

$$\Delta S = mc_s ln\frac{T_2}{T_1} = (4780\ g)(0.717\ J\ g^{\sim 1}\ K^{-1}) ln\frac{503\ K}{293\ K} = 1850\ J\ K^{-1}$$ ***+4 point***

5. (total 10 pts)

Estimate the pH of a 0.0100 M solution of ammonium formate in water at 25 °C. Formic acid, HCOOH, is the simplest organic acid and has $K_a = 10^{-3.7}$. For NH_4^+, $K_a = 10^{-9.3}$. Rationalize your answer.

.

(Answer)

Three equilibria are possible here; the reaction of the ammonium ion and formic acid with water, and the reaction of ammonium and formate ions.

$NH_4^+ + H_2O \rightleftarrows NH_3 + H_3O^+$ (1) $K_1 = K_a(NH_4^+) = 10^{-9.3}$

$HCOOH + H_2O \rightleftarrows HCOO^- + H_3O^+$ (2) . $K_2 = K_a(HCOOH) = 10^{-3.7}$

$NH_4^+ + HCOO^- \rightleftarrows NH_3 + HCOOH$ (3) K_3

Equation (3) = (1) - (2)

$K_3 = K_1 / K_2 = 10^{-9.3+3.7} = 10^{-5.6}$ ***+3 point***

$[NH_4^+] = [HCOO^-]$ and $[NH_3] = [HCOOH]$

Then $K_3 = \frac{[NH_3][HCOOH]}{[NH_4^+][HCOO^-]} = \frac{[HCOOH]^2}{[HCOO^-]^2} = 10^{-5.6}$

$\therefore \frac{[HCOOH]}{[HCOO^-]} = 10^{-2.8}$ ***+3 point***

From equation (2)

$$\therefore \frac{[HCOO^-][H_3O^+]}{[HCOOH]} = 10^{-3.7}$$

$\therefore [H_3O^+] = 10^{-3.7} \times \frac{[HCOOH]}{[HCOO^-]} = 10^{-3.7} \times 10^{-2.8} = 10^{-6.5}$ ***+3 point***

$\therefore$ pH = 6.5 ***+1 point***

Another answer

8 lines are the same as previous answer

Then $K_3 = \frac{[NH_3][HCOOH]}{[NH_4^+][HCOO^-]} = \frac{[NH_3]^2}{[NH_4^+]^2} = 10^{-5.6}$

$\therefore \frac{[NH_3]}{[NH_4^+]} = 10^{-2.8}$ ***+3 point***

$NH_3 + H_2O \rightleftarrows NH_4^+ + OH^-$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{K_W}{K_a} = \frac{10^{-14}}{10^{-9.3}} = 10^{-4.7}$$

$$\therefore [OH^-] = 10^{-4.7} \times \frac{[NH_3]}{[NH_4^+]} = 10^{-4.7} \times 10^{-.2.8} = 10^{-.7.5}$$

$\therefore [H_3O^+] = \frac{K_W}{[OH^-]} = \frac{10^{-14}}{10^{-7.5}} = 10^{-6.5}$ ***+3 point***

$\therefore$ pH = 6.5 ***+1 point***

6. (total 9 pts)

Identify the acid and base in each of these reactions (each 3pts):

(a) $2\ CaO + SiO_2 \rightarrow Ca_2SiO_4$

(b) $Ca_2SiO_4 + SiO_2 \rightarrow 2\ CaSiO_3$

(c) $Ca_2SiO_4 + CaO \rightarrow Ca_3SiO_5$

Answer

For each question, no partial point

(a) CaO (Base), SiO_2(Acid)

In the first reaction CaO donates O^{2-} to SiO_2 so CaO is the base, and SiO_2 is the acid.

(b) Ca_2SiO_4 (Base), SiO_2(Acid)

In the second reaction the SiO_2 again accepts an O^{2-} and is again the acid. It accepts the O^{2-} from

(c) Ca_2SiO_4 (Acid), CaO(base)

In the third reaction, the CaO donates O^{2-} to Ca_2SiO_4. The latter serves as an acid in this reaction, the opposite of its role in the second reaction.

7. (total 10 pts)

(a) (5 pts) Suppose 100.0 mL of a 0.0100 M $CaCl_2$ solution and 200.0 mL of a 0.0200 M Na_3PO_4 solution were mixed. K_{sp} of $Ca_3(PO_4)_2$ is 1.0×10^{-26}. Would a precipitate occur? Write the chemical equation and rationalize your answer.

(Answer)

The balanced chemical equation:

$3\ CaCl_2\ (aq) + 2\ Na_3PO_4\ (aq) \rightleftarrows Ca_3(PO_4)_2\ (s) + 6\ NaCl\ (aq)$ ***+1 point***

Net ionic form:

$3\ Ca^{2+}\ (aq) + 6\ Cl^-\ (aq) + 6\ Na^+\ (aq) + 2\ PO_4^{3-}\ (aq) \rightleftarrows Ca_3(PO_4)_2\ (s) + 6\ Na^+\ (aq) + 6\ Cl^-\ (aq)$

$3\ Ca^{2+}\ (aq) + 2\ PO_4^{3-}\ (aq) \rightleftarrows Ca_3(PO_4)_2\ (s)$

The concentration of the Ca^{2+} ions and the PO_4^{3-} ions resulting from the mixing of the two solutions:

$$[Ca^{2+}] = \frac{(0.100\ L)(0.010\ mol\ L^{-1})}{0.300\ L} = 0.00333\ M$$

$$[PO_4{}^{3+}] = \frac{(0.200\ L)(0.020\ mol\ L^{-1})}{0.300\ L} = 0.0133\ M$$ ***+1 point***

The solubility product quotient:

$Q = [Ca^{2+}]^3[PO_4^{3-}]^2 = [0.00333\ M]^3[0.0133\ M]^2 = 6.532 \times 10^{-12} > K_{sp} = 1.0 \times 10^{-26}$ ***+2 point***

$\therefore$ A precipitate of $Ca_3(PO_4)_2$ will form in this case. ***+1 point***

(b) (5 pts) What is the molar solubility of $Ca_3(PO_4)_2$ in water?

(Answer)

$Ca_3(PO_4)_2\ (s) \rightleftharpoons 3\ Ca^{2+}\ (aq) + 2\ PO_4^{3-}\ (aq)$

Reaction	$Ca_3(PO_4)_2$ (s) $\rightleftharpoons$	3 Ca^{2+} (aq) +	2 PO_4^{3-} (aq)
Initial		0	0
Change	-y	3y	2y
Equilibrium	-y	3y	2y

$K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2 = 1.0 \times 10^{-26} = (3y)^3(2y)^2$ ***+2 point***

$108\ y^5 = 1.0 \times 10^{-26}$

$y^5 = 1.0 \times 10^{-26} / 108 = 9.3 \times 10^{-29}$

$y = 2.5 \times 10^{-6}$

The molar solubility of $Ca_3(PO_4)_2$ is 2.5×10^{-6} M. ***- Full points for correct answer***

8. (total 9 pts, each 3 pts)

For each of the following ionic compounds, state whether the solubility will increase, decrease, or remain unchanged as a solution at pH 7 is made acidic.

(a) $SrCO_3$ (b) Hg_2Br_2 (c) MnS

Answer

(a) Solubility will increase as CO_3^{2-} reacts with H_3O^+ to give HCO_3^- .

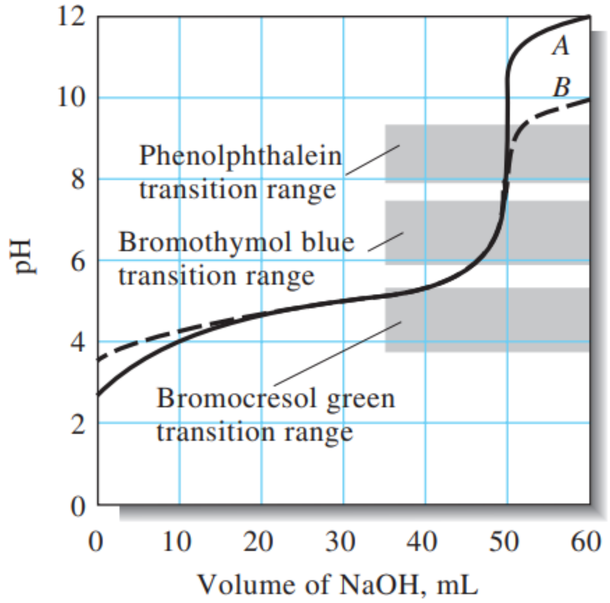
(b) Solubility will show little change because HBr is a strong acid.

(c) Solubility will increase as HS^- (from the dissolution of the MnS) reacts with H_3O^+ to give H_2S.

- Full points for correct answer

9. (total 12 pts)

The following is a titration curve of acetic acid with sodium hydroxide. One of the curves is titration of 0.1 M acid with 0.1 M base, and the other is for 0.001M acid with 0.001 M base. (pK_a of acetic acid: 4.75)



(a) (4 pts) Which concentration of acid/base does the curve A and curve B correspond to?

(b) (8 pts, each 2 pts) In the case of 0.1 M acetic with 0.1 M sodium hydroxide, calculate the pH at 45, 49, 50, 55 ml of NaOH.

Answer

The image was adopted from "Fundamentals of Analytical Chemistry, 9th edition" by Skoog et al

(a) A: 0.1 M of acid/base // B: 0.001M of acid/base (0 or 4 points)

(b) As the titration curve shows an equivalence point at 50 ml, the initial volume of 0.1 M acid is 50 ml.

At 45ml, pH = 5.70

$$\mathrm{pH} = 4.75 - \log_{10}\frac{5 - 4.5\ mmol}{4.5\ \mathrm{mmol}}$$

At 49ml, pH = 6.44

$$\mathrm{pH} = 4.75 - \log_{10}\frac{5 - 4.9\ mmol}{4.9\ \mathrm{mmol}}$$

At 50 ml, the pH is governed by the hydrolysis of the weak base AcO^-. pH = 8.73

At 55ml, the pH is governed by the excess $[OH^-]$. The additional hydroxy ion is 0.5 mmol, and the total volume of the solution is 105 ml. So, pH = 14 – pOH = 11.68

10. (total 10 pts, each 2.5 pts)

A galvanic cell consists of a cadmium cathode immersed in a $CdSO_4$ solution and a zinc anode immersed in a $ZnSO_4$ solution. A salt bridge connects the two half-cells.

The balanced equation of the cell is

$$Zn(s) + Cd^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cd(s)$$

(a) A current of 1.45 A is observed to flow for a period of 2.60 hours. How much charge passes through the circuit during this time? (2.5 pts)

(b) How many moles of electrons is this charge equivalent to? (2.5 pts)

(c) Calculate the change in mass of the zinc electrode. (2.5 pts)

(d) Calculate the change in mass of the cadmium electrode. (2.5 pts)

Answer

(a) The product of the (steady) current in amperes and the time in seconds is the charge in coulombs. It is 1.36×10^4 C.

(b) Dividing by the Faraday constant gives the chemical amount of electrons, 0.141 mol.

(c) Every 1 mol of electrons that passes through the cell oxidizes 1/2 mol of zinc. Hence 0.0703 mol of zinc is oxidized. This is 4.60 g of zinc and is the mass lost by the zinc electrode.

(d) Every 1 mol of electrons that passes through the cell reduces 1/2 mol of cadmium(II) ions. This is 0.0703 mol of Cd^{2+}, or 7.91 g of Cd^{2+}. This is the mass gained by the cadmium electrode.

Physical Constants

Avogadro's number	$N_A = 6.02214179 \times 10^{23}$ mol^{-1}
Bohr radius	$a_0 = 0.52917720859$ Å $= 5.2917720859 \times 10^{-11}$ m
Boltzmann's constant	$K_B = 1.3806504 \times 10^{-23}$ J K^{-1}
Electronic charge	$e = 1.602176487 \times 10^{-19}$ C
Faraday constant	$F = 96485.3399$ C mol^{-1}
Masses of fundamental particles:	
Electron	$m_e = 9.10938215 \times 10^{-31}$ kg
Proton	$m_P = 1.672621637 \times 10^{-27}$ kg
Neutron	$m_n = 1.674927211 \times 10^{-27}$ kg
Permittivity of vacuum	$\varepsilon_o = 8.854187817 \times 10^{-12}$ C^{-2} J^{-1} m^{-1}
Planck's constant	$h = 6.62606896 \times 10^{-34}$ J s
Ratio of proton mass to electron mass	$m_P / m_e = 1836.15267247$
Speed of light in a vacuum	c = 2.99792458×10^{8} m s^{-1} (exactly)
Standard acceleration of terrestrial gravity	$g = 9.80665$ m s^{-2} (exactly)
Universal gas constant	$R = 8.314472$ J mol^{-1} K^{-1} $= 0.0820574$ L atm mol^{-1} K^{-1}

Values are taken from the 2006 CODATA recommended values,
as listed by the National Institute of Standards and Technology.

Conversion factors

Ångström	1 Å= 10^{-10} m
Atomic mass unit	1 u = $1.660538782 \times 10^{-27}$ kg
	1 u = $1.492417830 \times 10^{-10}$ J = 931.494028 MeV (energy equivalent form $E = mc^2$)
Calorie	1 cal = 4.184 J (exactly)
Electron volt	1 eV = 1.602177×10^{-19} J = 96.485335 kJ mol^{-1}
Foot	1 ft = 12 in = 0.3048 m (exactly)
Gallon (U. S.)	1 gallon = 4 quarts = 3.785412 L (exactly)
Liter	1 L = 10^{-3} m^{-3} = 10^{3} cm^{3} (exactly)
Liter-atmosphere	1 L atm = 101.325 J (exactly)
Metric ton	1 t = 1000 kg (exactly)
Pound	1 lb = 16 oz = 0.4539237 kg (exactly)
Rydberg	1 Ry = $2.17987197 \times 10^{-18}$J = 1312.7136 kJ mol^{-1} = 13.60569193 eV
Standard atmosphere	1 atm = 1.01325×10^{5} Pa = 1.01325×10^{5} kg m^{-1} s^{-2} (exactly)
Torr	1 torr = 133.3224 Pa

PERIODIC TABLE OF THE ELEMENTS

http://www.ktf-split.hr/periodni/en/

GROUP NUMBERS IUPAC RECOMMENDATION (1985): 13 — GROUP NUMBERS CHEMICAL ABSTRACT SERVICE (1986): IIIA

ATOMIC NUMBER: 5 — RELATIVE ATOMIC MASS (1): 10.811 — SYMBOL: B — ELEMENT NAME: BORON

PERIOD	GROUP 1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIIIB	9 VIIIB	10 VIIIB	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1	1 1.0079 H HYDROGEN																	2 4.0026 He HELIUM
2	3 6.941 Li LITHIUM	4 9.0122 Be BERYLLIUM											5 10.811 B BORON	6 12.011 C CARBON	7 14.007 N NITROGEN	8 15.999 O OXYGEN	9 18.998 F FLUORINE	10 20.180 Ne NEON
3	11 22.990 Na SODIUM	12 24.305 Mg MAGNESIUM											13 26.982 Al ALUMINIUM	14 28.086 Si SILICON	15 30.974 P PHOSPHORUS	16 32.065 S SULPHUR	17 35.453 Cl CHLORINE	18 39.948 Ar ARGON
4	19 39.098 K POTASSIUM	20 40.078 Ca CALCIUM	21 44.956 Sc SCANDIUM	22 47.867 Ti TITANIUM	23 50.942 V VANADIUM	24 51.996 Cr CHROMIUM	25 54.938 Mn MANGANESE	26 55.845 Fe IRON	27 58.933 Co COBALT	28 58.693 Ni NICKEL	29 63.546 Cu COPPER	30 65.39 Zn ZINC	31 69.723 Ga GALLIUM	32 72.64 Ge GERMANIUM	33 74.922 As ARSENIC	34 78.96 Se SELENIUM	35 79.904 Br BROMINE	36 83.80 Kr KRYPTON
5	37 85.468 Rb RUBIDIUM	38 87.62 Sr STRONTIUM	39 88.906 Y YTTRIUM	40 91.224 Zr ZIRCONIUM	41 92.906 Nb NIOBIUM	42 95.94 Mo MOLYBDENUM	43 (98) Tc TECHNETIUM	44 101.07 Ru RUTHENIUM	45 102.91 Rh RHODIUM	46 106.42 Pd PALLADIUM	47 107.87 Ag SILVER	48 112.41 Cd CADMIUM	49 114.82 In INDIUM	50 118.71 Sn TIN	51 121.76 Sb ANTIMONY	52 127.60 Te TELLURIUM	53 126.90 I IODINE	54 131.29 Xe XENON
6	55 132.91 Cs CAESIUM	56 137.33 Ba BARIUM	57-71 La-Lu Lanthanide	72 178.49 Hf HAFNIUM	73 180.95 Ta TANTALUM	74 183.84 W TUNGSTEN	75 186.21 Re RHENIUM	76 190.23 Os OSMIUM	77 192.22 Ir IRIDIUM	78 195.08 Pt PLATINUM	79 196.97 Au GOLD	80 200.59 Hg MERCURY	81 204.38 Tl THALLIUM	82 207.2 Pb LEAD	83 208.98 Bi BISMUTH	84 (209) Po POLONIUM	85 (210) At ASTATINE	86 (222) Rn RADON
7	87 (223) Fr FRANCIUM	88 (226) Ra RADIUM	89-103 Ac-Lr Actinide	104 (261) Rf RUTHERFORDIUM	105 (262) Db DUBNIUM	106 (266) Sg SEABORGIUM	107 (264) Bh BOHRIUM	108 (277) Hs HASSIUM	109 (268) Mt MEITNERIUM	110 (281) Uun UNUNNILIUM	111 (272) Uuu UNUNUNIUM	112 (285) Uub UNUNBIUM		114 (289) Uuq UNUNQUADIUM				

LANTHANIDE

6	57 138.91 La LANTHANUM	58 140.12 Ce CERIUM	59 140.91 Pr PRASEODYMIUM	60 144.24 Nd NEODYMIUM	61 (145) Pm PROMETHIUM	62 150.36 Sm SAMARIUM	63 151.96 Eu EUROPIUM	64 157.25 Gd GADOLINIUM	65 158.93 Tb TERBIUM	66 162.50 Dy DYSPROSIUM	67 164.93 Ho HOLMIUM	68 167.26 Er ERBIUM	69 168.93 Tm THULIUM	70 173.04 Yb YTTERBIUM	71 174.97 Lu LUTETIUM

ACTINIDE

7	89 (227) Ac ACTINIUM	90 232.04 Th THORIUM	91 231.04 Pa PROTACTINIUM	92 238.03 U URANIUM	93 (237) Np NEPTUNIUM	94 (244) Pu PLUTONIUM	95 (243) Am AMERICIUM	96 (247) Cm CURIUM	97 (247) Bk BERKELIUM	98 (251) Cf CALIFORNIUM	99 (252) Es EINSTEINIUM	100 (257) Fm FERMIUM	101 (258) Md MENDELEVIUM	102 (259) No NOBELIUM	103 (262) Lr LAWRENCIUM

(1) Pure Appl. Chem., 73, No. 4, 667-683 (2001)
Relative atomic mass is shown with five significant figures. For elements have no stable nuclides, the value enclosed in brackets indicates the mass number of the longest-lived isotope of the element.
However three such elements (Th, Pa, and U) do have a characteristic terrestrial isotopic composition, and for these an atomic weight is tabulated.

Editor: Aditya Vardhan (adivar@nettlinx.com)