2017 FALL Semester Midterm Examination
For General Chemistry I

Date: October 18 (Wed), Time Limit: 19:00 ~ 21:00

Write down your information neatly in the space provided below; print your Student ID in the upper right corner of every page.

Professor Name	Class	Student I.D. Number	Name

Problem	points	Problem	points	TOTAL pts
1	/10	**6**	/10	**/100**
2	/10	**7**	/6	
3	/10	**8**	/10	
4	/10	**9**	/10	
5	/10	**10**	/14	

** This paper consists of 9 sheets with 10 problems (page 7 - 8: constants & periodic table, page 9: claim form). Please check all page numbers before taking the exam. Write down your work and answers in the Answer sheet. Please write down the unit of your answer when applicable. You will get 30% deduction for a missing unit.

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

1. Period, Location, and Procedure

1) Return and Claim Period: ***October 23 (Mon, 19: 00 ~ 20:00 p.m.)***
2) ***Location: Room for quiz sessions***
3) Procedure:

Rule 1: Students cannot bring their own writing tools into the room. (Use a pen only provided by TA)

Rule 2: With or without claim, you must submit the paper back to TA. (Do not go out of the room with it)

If you have any claims on it, you can submit the claim paper with your opinion. After writing your opinions on the claim form, attach it to your mid-term paper with a stapler. Give them to TA.

(The claim is permitted only on the 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 26 (Thu) – Oct 27 (Fri)
2) Procedure: During this period, you can check final score of the examination *on the website* again.

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

1. (total 10 pts: each 2 pts for a right answer, -1 pt for a wrong answer, 0 pt for no answer)

Read the following statements and verify whether these are “TRUE (T)” or “FALSE (F)”.

(a) For neutral atoms, second ionization energy is always higher than the first ionization energy (except Hydrogen atom)

(Answer)

(b) Probability of finding the particle in a region is proportional to the value of $|\Psi|^2$.

(Answer)

(c) For the energy of a wavefunction to be quantized, the wavefunction must have boundary conditions

(Answer)

(d) Atomic radius is defined as half the distance between the centers of neighboring ions in an ionic solid.

(Answer)

(e) The relative energy order of atomic orbitals follows … 3s < 3p < 3d < 4s < 4p….

(Answer)

2. (total 10 pts)

He^+ ions are observed in stellar atmospheres. Use the Bohr model to calculate the radius and the energy of He^+ in the n = 5 state. Express the following results in SI units.

(a) [5 pts] How much energy would be required to remove the electrons from 1 mol of He^+ in this state?

(Answer)

(b) [5 pts] What frequency and wavelength of light would be emitted in a transition from the n = 5 to the n = 3 state of this ion?

(Answer)

3. (total 10 pts)

(a) [5 pts] Write ground-state electron configurations for the ions Li^-, Al^{3+}, S^-, Ar^+, and Te^-.

(Answer)

(b) [5 pts] Predict whether these ions are diamagnetic or paramagnetic.

(Answer)

4. (total 10 pts)

(a) [5 pts] The wavelength of the radiation emitted when the outermost electron of aluminum falls from the 4*s* state to the ground state is about 395 nm. Calculate the energy separation (in joules) between these two states in the Al atom.

(Answer)

(b) [5 pts] When the outermost electron in aluminum falls from the 3*d* state to the ground state, the radiation emitted has a wavelength of about 310 nm. Draw an energy-level diagram of the states and transitions discussed here and in (a). Calculate the separation (in joules) between the 3*d* and 4*s* states in aluminum. Indicate clearly which has higher energy.

(Answer)

5. (total 10 pts)

How many radial nodes and how many angular nodes does each of the orbitals have?

(a) [5 pts] $\mathrm{n} = 3, \ell = 2$

(Answer)

(b) [5 pts] $n = 7, \ell = 4$

(Answer)

6. (total 10 pts: each 2 pts)

Which atom or ion in each pair has larger ionization energy? Justify your answer with their electronic configurations.

(a) Na, Na^+

(Answer)

(b) N, O

(Answer)

(c) F, Cl

(Answer)

Predict whether the atoms below are paramagnetic or diamagnetic. Justify your answer with their electronic configurations.

(d) Cr

(Answer)

(e) Zn

(Answer)

7. (total 6 pts) Find out the most favorable Lewis diagrams with all resonance structures for the following molecules and the corresponding VSEPR structures with appropriate steric numbers.

(a) [3 pts] CH_2Cl_2

(Answer)

(b) [3 pts] MnO_4^-

(Answer)

8. (total 10 pts) It takes 334 J to melt 1 g of ice at 0°C.

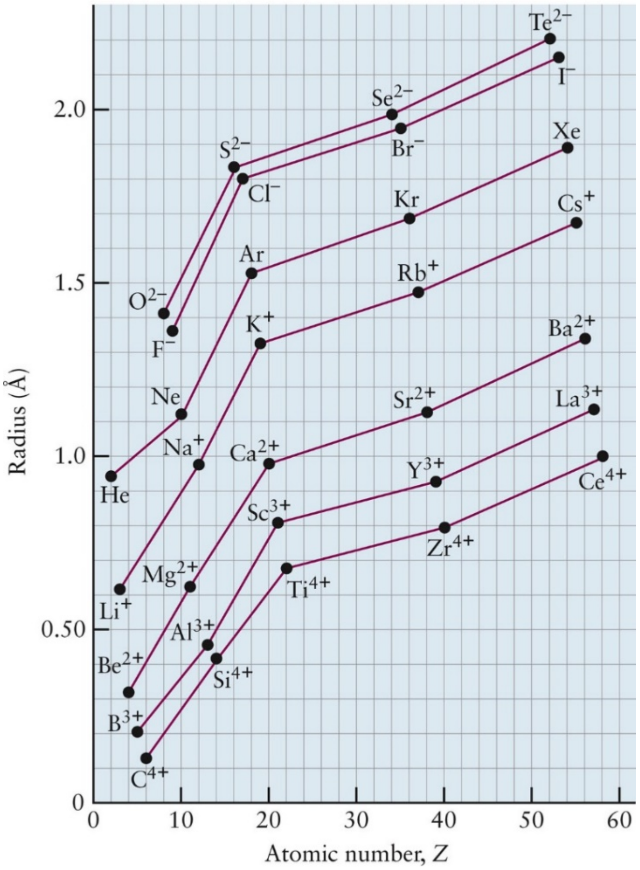
(a) [5 pts] How many photons at 660 nm must be absorbed to melt 5.0 X 10^2 g of ice?

(Answer)

(b) [5 pts] On average, how many H_2O molecules does one photon convert from ice to water?

(Answer)

9. (total 10 pts)



The left figure shows the radius of atoms and ions as a function of atomic number. There is an abrupt change in the rate of increase in the atomic radius, for example, as going from Ar to Kr.

(a) [5 pts] Explain its origin in terms of different <u>shielding effects of orbitals</u>.

(Answer)

(b) [5 pts] What is the <u>Lanthanide contraction</u>? Explain its origin in terms of the <u>shielding effect of f orbitals</u>.

(Answer)

10. (total 14 pts)

An orbital energy of many electron atoms can be expressed with effective nuclear charge under the Hartree approximation as follows.

$$\epsilon_{\boldsymbol{n}} \approx -\frac{[Z_{eff}(\boldsymbol{n})]^{\mathbf{2}}}{\boldsymbol{n}^{\mathbf{2}}} \text{ Ry}$$

Using the following effective nuclear charges of N (1s: 6.00, 2s: 4.00, 2p: 3.00), answer the questions below.

(a) [3 pts] Calculate all possible first ionization energies in the unit of Ry according to the Koopmans's approximation.

(Answer)

(b) [3 pts] Calculate the expected kinetic energies in the unit of Ry when the atom is irradiated by X-ray with 100 Ry. Assume that the second ionization energies are much larger than the radiation energy.

(Answer)

(c) [4 pts] Given that the electronic states are frozen upon the ionization, calculate the first electronic excitation energy of N^+ in the unit of Ry.

(Answer)

(d) [4 pts] If an external magnetic field ***B*** is applied to N, how many first ionization energies do you expect? Justify your answer. Ignore the effect of electron spins.

(Answer)

Use the following equations to solve problems.

$$r_n = -\frac{n^2}{Z}a_0, \qquad a_0 = 0.529 \text{ Å}$$

$$E_n = \frac{n^2h^2}{8mL^2}, \qquad n = 1, 2,3 \ldots$$

$$E_n = -\frac{Z^2e^4m_e}{8\varepsilon_0^2n^2h^2}, \qquad n = 1, 2,3 \ldots$$

$$E_n = -\frac{Z^2}{n^2}(Rydberg)$$

$$E = h\nu = h\frac{c}{\lambda}$$

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}
Electron charge	$e = 1.602176487 \times 10^{-19}$ C
Faraday constant	$F = 96{,}485.3399$ 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	$\epsilon_0 = 8.854187817 \times 10^{-12}$ 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	$c = 2.99792458 \times 10^8$ 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 from $E = mc^2$)
Calorie	1 cal = 4.184 J (exactly)
Electron volt	1 eV $= 1.602177 \times 10^{-19}$ J
	= 96.485335 kJ mol
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
	= 13.60569193 eV
Standard atmosphere	1 atm $= 1.01325 \times 10^5$ Pa
	$= 1.01325 \times 10^5$ 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

Period														
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

Period															
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)

Claim Form for General Chemistry Examination

Page (/   )

Class:__________, Professor Name:___________, I.D.# :_____________, Name:_______________________

If you have any claims on the marked paper, please write down them on this form and ***submit this with your paper in the assigned place***. (And this form should be attached ***on the top of the marked paper with a stapler***.) Please, ***copy this sheet if you need more before use***.

By Student		By TA	
Question #	Claims	Accepted? Yes(√) or No(√)	
		Yes: ☐	No: ☐
		Pts (+/-)	Reasons

2017 FALL Semester Midterm Examination

Answers

1. (total 10 pts: each 2 pts for a right answer, -1 pt for a wrong answer, 0 pt for no answer)

Read the following statements and verify whether these are "TRUE (T)" or "FALSE (F)".

(a) For neutral atoms, second ionization energy is always higher than the first ionization energy (except Hydrogen atom)

(Answer)

T

(b) Probability of finding the particle in a region is proportional to the value of $|\Psi|^2$.

(Answer)

T

(c) For the energy of a wavefunction to be quantized, the wavefunction must have boundary conditions

(Answer)

T

(d) Atomic radius defined as half the distance between the centers of neighboring ions in an ionic solid.

(Answer)

F

(e) The relative energy order of atomic orbitals follows … 3s < 3p < 3d < 4s < 4p….

(Answer)

F

2. (total 10 pts)

He^+ ions are observed in stellar atmospheres. Use the Bohr model to calculate the radius and the energy of He^+ in the n=5 state. Express following results in SI units.

(Chapter 4-20)

(a) [5 pts] How much energy would be required to remove the electrons from 1 mol of He^+ in this state?

(Answer)

According to the Bohr model, the radius of a one-electron atom or ion is

$$r_n = \frac{n^2}{Z}a_0 = \frac{n^2}{Z}(5.29 \times 10^{-11} m)$$

Substitution of Z=2 (for helium) and n=5 gives r =6.61 x 10^{-10} m. The energy of an allowed state of a one-electron atom or ion is

$$E_n = -\frac{Z^2}{n^2}(2.18 \times 10^{-18} J)$$

For He^+ ion in the n=5 state, this energy equals -3.49 x 10^{-19} J. Removing the electron means changing the energy of the ion to E = 0. The change in energy is this final value minus the initial value, or +3.49 x 10^{-19}. For a mole of atoms the energy change is Avogadro`s number times larger or 210 kJ mol^{-1}.

(5.0 ; avogadro number 2.0 calculation 1.0 answer 2.0)

(b) [5 pts] What frequency and wavelength of light would be emitted in a transition from the n=5 to the n=3 state of this ion?

(Answer)

The energy of a He^+ ion in the n=3 state is -9.69×10^{-19} J. The change in energy of a He^+ ion in the 5 ->3 transition equals

$$\Delta E = E_3 - E_5 = -9.69\times10^{-19} J - (-3.49\times10^{-19} J) = -6.20\times10^{-19} J$$

(partial point 1.0 if you have wrong answers of wavelength and energy)

The transition gives off energy, as shown by the negative ΔE. The frequency of the photon that carries away this energy is 9.36×10^{14} s^{-1} **(2.5 ;procedure 1.0)** and the wavelength is 320 nm. **(2.5 ;procedure 1.0)**

3. (total 10 pts) (Chapter 5-18)
(a) [5 pts] Write ground-state electron configurations for the ions Li^-, Al^{3+}, S^-, Ar^+, and Te^-.

(Answer)

Species	Ground state configuration
Li^-	$1s^2 2s^2$
Al^{3+}	$1s^2 2s^2 2p^6$
S^-	$1s^2 2s^2 2p^6 3s^2 3p^5$
Ar^+	$1s^2 2s^2 2p^6 3s^2 3p^5$
Te^-	$[Kr]4d^{10} 5s^2 5p^5$

Each 1 pt

(b) [5 pts] Predict whether these ions are diamagnetic or paramagnetic.

(Answer)

Li^-, Al^{3+}: Diamagnetic

S^-, Ar^+, and Te^-.Paramagnetic

Each 1 pt for right answer

4. (total 10 pts) (Chapter 5-56)
(a) [5 pts] The wavelength of the radiation emitted when the outermost electron of aluminum falls from the 4*s* state to the ground state is about 395 nm. Calculate the energy separation (in joules) between these two states in the Al atom.

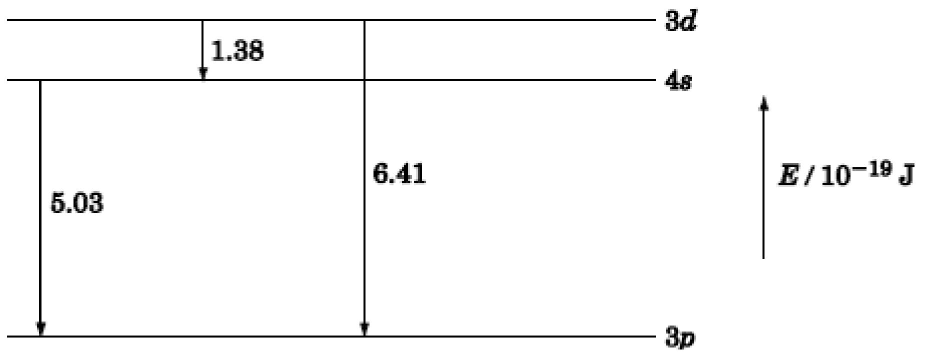
(Answer)

$$\Delta E = \frac{hc}{\lambda} = \frac{(6.626\times10^{-34}\ \text{J s})(2.998\times10^{8}\ \text{m s}^{-1})}{395\times10^{-9}\ \text{m}} = 5.03\times10^{-19}\ \text{J}$$

+ 5 pts

(b) [5 pts] When the outermost electron in aluminum falls from the 3*d* state to the ground state, the radiation emitted has a wavelength of about 310 nm. Draw an energy-level diagram of the states and transitions discussed here and in (b). Calculate the separation (in joules) between the 3*d* and 4*s* states in aluminum. Indicate clearly which has higher energy.

(Answer)



The separation is 1.38×10^{-19} J, the 3*d* state lying above the 4*s* state.

Right calculation for 310 nm energy: **+3 pts.**
Right calculation for energy separation **+2 pts**

5. (total 10 pts)

How many radial nodes and how many angular nodes does each of the orbitals have?

(Chapter 5-4)

(a) [5 pts] $n = 3, \ell = 2$

(Answer)

Number of radial node = 0 **(2.5 pts)**

Number of angular node = 2 **(2.5pts)**

(b) [5 pts] $n = 7, \ell = 4$

(Answer)

Number of radial node = 2 **(2.5 pts)**

Number of angular node = 4 **(2.5 pts)**

6. (total 10 pts: 2 pts for each)

Which atom or ion in each pair has larger ionization energy? Justify your answer with their electronic configurations.

(a) Na, Na^+

(Answer)

Na^+, **+1 pt for right answer**

Na: [Ne]$3s^1$, Na^+: [He]$2s^2 2p^6$; Na satisfies octet rule when it loses an electron, it means that Na has very small IE. **+1 pt for right electron configuration**

(b) N, O

(Answer)

N, **+1 pt for right answer**

N: [He]$2s^2 2p^3$, O: [He]$2s^2 2p^4$; O has 1 electron pair in one of 2p orbital so it is less stable than 2p of N because of electron repulsion. **+1 pt for right electron configuration**

(c) F, Cl

(Answer)

F, **+1 pt for right answer**

F: [He]$2s^2 2p^5$, Cl:[Ne]$3s^2 3p^5$; Both F and Cl has same number of valence electrons, but the energy of 2p is more stable than 3p. **+1 pt for right electron configuration**

Predict whether the atoms below are paramagnetic or diamagnetic. Justify your answer with their electronic configurations.

(d) Cr

(Answer)

Paramagnetic. **+1 pt for right answer** Cr: [Ar]$4s^1 3d^5$, **+1 pt for right electron configuration**

(e) Zn

(Answer)

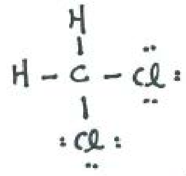
Diamagnetic. **+1 pt for right answer** Zn: [Ar]$4s^2 3d^{10}$ **+1 pt for right electron configuration**

7. (total 6 pts) Find out the most favorable Lewis diagrams with all resonance structures for the following molecules and the corresponding VSEPR structures with appropriate steric numbers.

(a) [3 pts] CH_2Cl_2

(Answer)

(a)



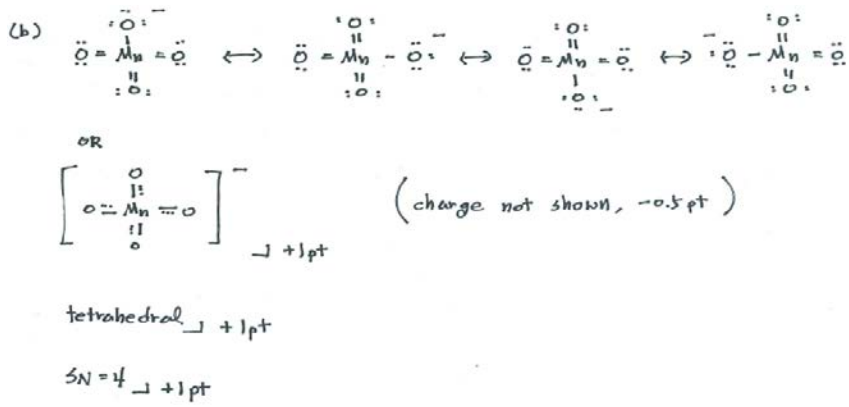
⌋ +1pt

distorted tetrahedral ⌋ +1 pt ('distorted' missing, -0.5 pt)

SN = 4 ⌋ +1 pt

(b) [3 pts] MnO_4^-

(Answer)



8. (total 10 pts) It takes 334 J to melt 1 g of ice at 0°C.

(a) [5 pts] How many photons at 660 nm must be absorbed to melt 5.0 X 10^2 g of ice?

(Answer)

The amount of energy that must be absorbed to melt 5.0 X 10^2 g of ice is

(5.0 X 10^2 g) X (334 J g^{-1}) = 1.67 X 10^5 J **+2 pts for right answer**

The energy of 1 photon at 660 nm is

$$h\nu = \frac{hc}{\lambda} = \frac{(6.626\times10^{-34}\,Js)(3.00\times10^{8}\,ms^{-1})}{660\times10^{-9}\,m} = 3.012\times10^{-19}\,J$$ **+2 pts for right answer**

so that the number of photons required to melt the water is

$$\frac{1.67\times10^{5}\,J}{3.012\times10^{-19}\,J} = 5.54\times10^{23}$$ **+1 pt for right answer**

(reduction by 0.5 pt if you have wrong numbers for each partial point)

(b) [5 pts] On average, how many H_2O molecules does one photon convert from ice to water?

(Answer)

The number of H_2O molecules converted in the 5.0 X 10^2 g sample from ice to water is

$$\frac{5.0\times10^{2}\,g}{18.0\,g\text{mol}^{-1}}\frac{6.022\times10^{23}}{1\text{mol}} = 1.67\times10^{25}$$

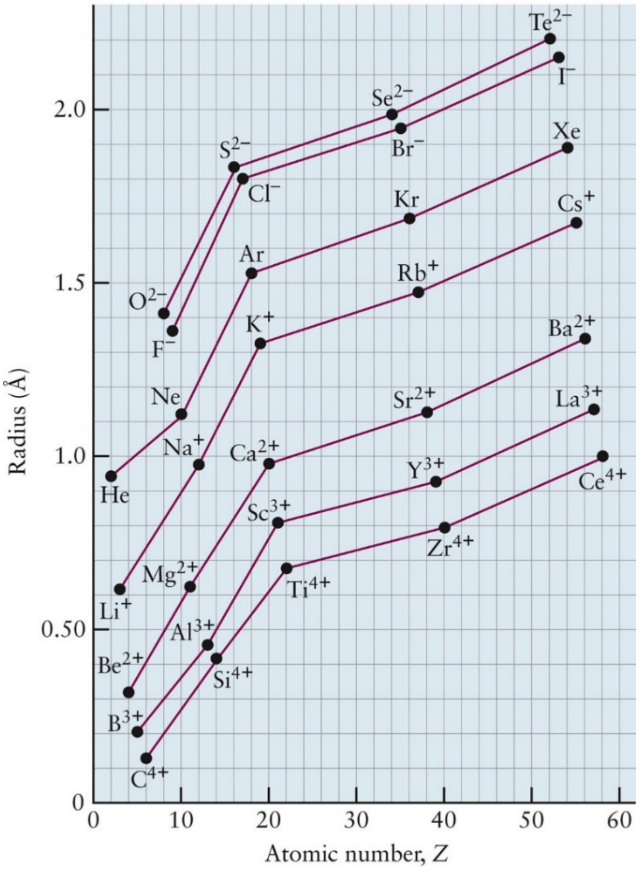
Since it took 5.54 X 10^{23} photons to melt the entire sample, the number of H_2O molecules converted from ice to water by 1 photon is

$$\frac{1.67\times10^{25}}{5.54\times10^{23}} = 30$$

(Reduction by 1.0 pt if you did minor calculation mistake with (or without) wrong answer from (a) with Right Formula)

(if the formula is wrong, get 0 pt)

9. (total 10 pts)



The left figure shows the atomic radius of atoms and ions as a function of atomic number. There is an abrupt change in the rate of increase in the atomic radius, for example, as going from Ar to Kr.

(a) [5 pts] Explain its origin in terms of different shielding effects of orbitals.

(Answer)

The abrupt change in the rate of increase in the atomic radius is due to the filling of the d orbitals. **+2.5 pts for right answer**

The d orbitals are much more diffuse/sharp compared to the s,p orbitals, thereby are much less effective in screening/shielding the nuclear charge. **+2.5 pts for right answer**

(b) [5 pts] What is the Lanthanide contraction? Explain its origin in terms of the shielding effect of f orbitals.

(Answer)

The 'Lanthanide contraction' is the greater-than-expected decrease in atomic radii of the elements in the lanthanide series. **+2.5 pts for right answer**

The effect results from poor screening/shielding of nuclear charge by 4f orbitals. **+2.5 pts for right answer**

10. (total 14 pts)

An orbital energy of many electron atoms can be expressed with effective nuclear charge under the Hartree approximation as follows.

$$\epsilon_n \approx -\frac{[Z_{eff}(n)]^2}{n^2} \text{ Ry}$$

Using the following effective nuclear charges of N (1s: 6.00, 2s: 4.00, 2p: 3.00), answer the questions below.

(a) [3 pts] Calculate all possible first ionization energies in the unit of Ry according to the Koopmans's approximation.

(Answer)

IE = 0 − $\epsilon_n = -\epsilon_n$

$IE_{1s} = -\epsilon_{1s} = \frac{6.00^2}{1^2}$ = 36 Ry **+1 pt for right answer**

$IE_{2s} = -\epsilon_{2s} = \frac{4.00^2}{2^2}$ = 4 Ry **+1 pt for right answer**

$IE_{2p} = -\epsilon_{2p} = \frac{3.00^2}{2^2}$ = 2.25 Ry **+1 pt for right answer**

(b) [3 pts] Calculate the expected kinetic energies in the unit of Ry when the atom is irradiated by X-ray with 100 Ry. Assume that the second ionization energies are much larger than the radiation energy.

(Answer)

$\mathrm{IE} = E_{photon} - KE_{electron}$

$KE_{electron} = E_{photon} - IE$

KE_{1s} = 100 Ry – 36 Ry = 64 Ry **+1 pt for right answer**

KE_{2s} = 100 Ry – 4 Ry = 96 Ry **+1 pt for right answer**

KE_{3s} = 100 Ry – 2.25 Ry = 97.75 Ry **+1 pt for right answer**

(c) [4 pts] Given that the electronic states are frozen upon the ionization, calculate the first electronic excitation energy of N^+ in the unit of Ry.

(Answer)

First electronic excitation energy = The smallest energy required to excite an electron.

N^+ = [He]$2s^2 2p^2$, 2 possible excitation available. 1) [He]$2s^2 2p^2$->[He]$2s^1 2p^3$, 2) [He]$2s^2 2p^2$->$1s^1 2s^2 2p^3$

Since 1) has lower excitation energy,

$E_{2s\to2p} = \epsilon_{2p} - \epsilon_{2s}$ = - 2.25 Ry – (- 4 Ry) = 1.75 Ry **+4 pts for right answer**

(d) [4 pts] If an external magnetic field ***B*** is applied to N, how many first ionization energies do you expect? Justify your answer. Ignore the effect of electron spins.

(Answer)

Orbital energy only depends on principle quantum number n. However, magnetic quantum number m affects energy when there is an external magnetic field. **+1 point for explanation (if answer is wrong)**

1s = (n, l, m) = (1, 0, 0)

2s = (n, l, m) = (2, 0, 0)

2p = (n, l, m) = (2, 1, -1), (2, 1, 0), (2, 1, 1) -> 3 different energies when external magnetic field exists.

Therefore, 5 first ionization energies are possible. **+4 points for right answer**

2017 FALL Semester Final Examination
For General Chemistry I

Date: December 13 (Wed), Time Limit: 19:00 ~ 21:00

Write down your information neatly in the space provided below; print your Student ID in the upper right corner of every page.

Professor Name	Class	Student I.D. Number	Name

Problem	points	Problem	points	TOTAL pts
1	/10	**6**	/10	**/100**
2	/10	**7**	/10	
3	/10	**8**	/10	
4	/10	**9**	/10	
5	/10	**10**	/10	

** This paper consists of 12 sheets with 10 problems (page 10 - 11: constants & periodic table, page 12: claim form). Please check all page numbers before taking the exam. Write down your work and answers in the Answer sheet.

Please write down the unit of your answer when applicable. You will get 30% deduction for a missing unit.

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

1. Period, Location, and Procedure

1) Return and Claim Period: ***December 15 (Fri, 12: 00 ~ 14:00 p.m.)***
2) ***Location: Room 201, E11(Creative Learning bldg.)***
3) Procedure:

Rule 1: Students cannot bring their own writing tools into the room. (Use a pen only provided by TA)

Rule 2: With or without claim, you must submit the paper back to TA. (Do not go out of the room with it)

If you have any claims on it, you can submit the claim paper with your opinion. After writing your opinions on the claim form, attach it to your mid-term paper with a stapler. Give them to TA.

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

2. Final Confirmation

1) Period: Dec 16 (Sat) – Dec 17 (Sun)
2) Procedure: During this period, you can check final score of the examination *on the website* again.

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

1. (total 10 pts: each 2 pts for a right answer, -1 pt for a wrong answer, 0 pt for no answer)
Read the following statements and verify whether these are "TRUE (T)" or "FALSE (F)".

(a) The LCAO method includes an ionic contribution to the bond, while the VB method does not.
(Answer)

(b) In real gases, repulsive interaction reduces pressure with respect to the ideal case, while attractive interaction increases volume
(Answer)

(c) In ideal gas behavior, each translation degree of freedom contributes RT/2, each vibrational degree of freedom contributes RT/2, and each rotational degree of freedom contributes RT to the internal energy.
(Answer)

(d) At constant T and P, the process will be reversible when $\Delta G_{sys} = 0$ but $\Delta S_{sys} > 0$.
(Answer)

(e) In the phase diagram, both the negative and positive slope for solid/liquid line is possible.
(Answer)

2. (total 10 pts, each 2.5 pts) Draw a Lewis electron dot diagram for each of the following molecules and ions. Formulate the hybridization for the central atom in each case and give the molecular geometry.

(a) BF_3
(Answer)

(b) CS_2
(Answer)

(c) PH_3

(Answer)

(d) CH_3^+

(Answer)

3. (total 10 pts) Carbon dioxide is liberated by the reaction of aqueous hydrochloric acid with calcium carbonate:

$$CaCO_3(s) + 2\ H^+(aq) \rightarrow Ca^{2+}(aq) + CO_2(g) + H_2O(\ell)$$

A volume of 722 mL $CO_2(g)$ is collected over water at 20 ℃ and a total pressure of 0.9963 atm. At this temperature, water has a vapor pressure of 0.0231 atm. Calculate the mass of calcium carbonate that has reacted, assuming no losses of carbon dioxide.

(Answer)

4. (total 10 pts) The normal boiling point of liquid ammonia is 240 K; the enthalpy of vaporization at that temperature is 23.4 kJ mol^{-1}. The heat capacity of gaseous ammonia at constant pressure is 38 J mol^{-1} K^{-1}.

(a) [4 pts] Calculate q, w, ΔH, and ΔU for the following change in state:

$$2.00 \text{ mol } NH_3 \ (l, 1 \ atm, 240 \ K) \longrightarrow 2.00 \ mol \ NH_3 \ (g, 1 \ atm, 298 \ K)$$

Assume that the gas behaves ideally and that the volume occupied by the liquid is negligible.

(Answer)

(b) [6 pts] Calculate the entropy of vaporization of NH_3 at 240 K

(Answer)

5. (total 10 pts) A certain amount of NOBr(g) is sealed in a flask, and the temperature is raised to 350K. The following equilibrium is established:

$$NOBr(g) \rightleftharpoons NO(g) + \frac{1}{2}\ Br_2\ (g)$$

The total pressure in the flask when equilibrium is reached at this temperature of 0.675 atm, and the vapor density is 2.219 g L^{-1}. Molecular weight of NOBr is 109.91 g mol^{-1}.

(a) [6 pts] Calculate the partial pressure of each species at equilibrium.

(Answer)

(b) [4 pts] Calculate the equilibrium constant at this temperature.

(Answer)

6. (total 10 pts) Consider BO (boron-oxygen) and the effect of adding an electron, $\mathrm{BO} + \mathrm{e}^{-} \rightarrow \mathrm{BO}^{-}$.

(a) [5 pts] Write the <u>molecular electronic configurations</u> for BO and BO^{-}.

(Answer)

(b) [5 pts] Assess the effect of adding an electron on the <u>bond length</u> and <u>strength</u> of the molecule BO and <u>explain why.</u>

(Answer)

7. (total 10 pts) The partial pressure of oxygen in a mixture of oxygen and hydrogen is 0.200 atm, and that of hydrogen is 0.800 atm. (R = 0.08206 L atm mol^{-1} K^{-1}, Molecular mass H_2O = 18.02 g mol^{-1})

(a) [3 pts] How many molecules of oxygen are in a 1.500-L container of this mixture at 40°C? (The unit uses the mole)

(Answer)

(b) [3 pts] How many molecules of hydrogen are in a 1.500-L container of this mixture at 40°C? (The unit uses the mole)

(Answer)

(c) [4 pts] If a spark is introduced into the container, how many grams of water will be produced?

$$2\ H_2\ (g) + O_2\ (g) \rightarrow 2\ H_2O(\ell)$$

(Answer)

8. (total 10 pts) The combustion of nitromethane is used as a fuel, and the reaction is as follow:

$$CH_3NO_2(l) + O_2\ (g) \rightarrow CO_2\ (g) + \ N_2\ (g) + H_2O\ (g)\ \ \ldots\ldots\ldots\ldots\ldots(unbalanced)$$

(a) [6 pts] Calculate the standard enthalpy change (ΔH°) for nitromethane using the following data table. The ΔH°_{rxn} for the balanced reaction is -1288.5 kJ.

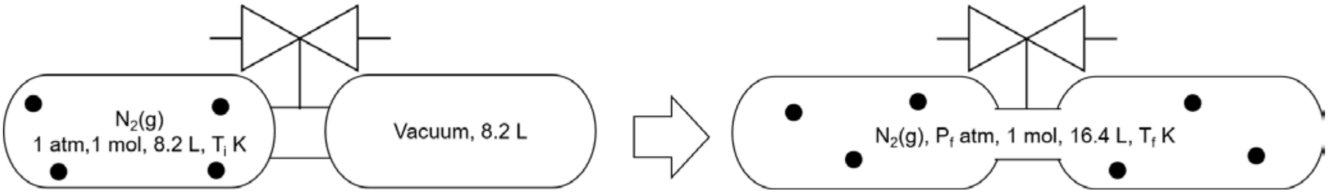
Substance	ΔH°_{f} (25°C) kJ/mol	S°(25°C) J/K·mol	ΔG°_{f} (25°C) kJ/mol	C_p (25°C) J/K·mol
$CO_2\ (g)$	-393.51	213.63	-394.36	37.11
$H_2O\ (g)$	-241.82	188.72	-228.59	35.58

(Answer)

(b) [4 pts] A 25.0L flask filled with nitromethane and O_2, is heated to 100℃. After the reaction is complete, the total pressure of all the gas inside the flask is 125 atm at the temperature. If the mole fraction of nitrogen ($x_{nitrogen}$) is 0.2 after the reaction is complete, what mass of nitrogen was produced?

(Answer)

9. (total 10 pts) Consider the free expansion of 1 mol nitrogen gas(T = T_i) from 8.2 L to 16.4 L in an isolated container system. Assume that N_2 gas behaves like an ideal gas.



(a) [3 pts] Calculate T_i, T_f, P_f.

(Answer)

(b) [4 pts] Calculate the q, w, ΔH, and ΔU for this process.

(Answer)

(c) [3 pts] Distinguish and explain why whether this process is reversible or irreversible, and spontaneous or nonspontaneous. (Hint: $\Delta S = nR\ln\frac{V_f}{V_i}$ in free expansion)

(Answer)

10. (total 10 pts) Consider the following chemical reactions and their equilibrium constants.

Eq 1. $A(g) \rightleftharpoons B(g) + C(g)$: $K_1 = 1/4$

Eq 2. $B(g) \rightleftharpoons D(g) + C(g)$: $K_2 = 3$

Eq 3. $A(g) \rightleftharpoons D(g) + 2C(g)$: $K_3 = ?$

At the first equilibrium, suppose that the concentrations of the species A and B are [A] = 4 and [B] = 1.

(a) [3 pts] Calculate the concentrations of the other species at the equilibrium and K_3.

(Answer)

(b) [4 pts] The concentration of the species B has been increased abruptly up to [B] = 2 under the constant volume and temperature. Guess whether the concentration of C is going to increase at the new equilibrium or not? Justify your answer.

(Answer)

(c) [3 pts] Propose a way to quantitatively determine the concentration of C at the new equilibrium.

(Answer)

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}
Electron charge	$e = 1.602176487 \times 10^{-19}$ C
Faraday constant	$F = 96{,}485.3399$ 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	$\epsilon_0 = 8.854187817 \times 10^{-12}$ 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	$c = 2.99792458 \times 10^8$ 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 from $E = mc^2$)
Calorie	1 cal = 4.184 J (exactly)
Electron volt	1 eV = 1.602177×10^{-19} J
	= 96.485335 kJ mol
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
	= 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 (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

PERIOD															
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

PERIOD															
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@netlinx.com)

<u>Claim Form for General Chemistry Examination</u>

Page (/)

Class:___________, Professor Name:____________, I.D.# :______________, Name:_________________________

If you have any claims on the marked paper, please write down them on this form and ***submit this with your paper in the assigned place***. (And this form should be attached ***on the top of the marked paper with a stapler***.) Please, ***copy this sheet if you need more before use***.

By Student		By TA	
Question #	Claims	Accepted? Yes(√) or No(√)	
		Yes: ☐	No: ☐
		Pts (+/-)	Reasons

2017 FALL Semester Final Examination

Answers

1. (total 10 pts: each 2 pts for a right answer, -1 pt for a wrong answer, 0 pt for no answer)

Read the following statements and verify whether these are “TRUE (T)” or “FALSE (F)”.

(a) The LCAO method includes an ionic contribution to the bond, while the VB method does not.

(Answer)

T

(b) In real gases, repulsive interaction reduces pressure with respect to the ideal case, while attractive interaction increases volume

(Answer)

F

(c) In ideal gas behavior, each translation degree of freedom contributes RT/2, each vibrational degree of freedom contributes RT/2, and each rotational degree of freedom contributes RT to the internal energy.

(Answer)

F

(d) At constant T and P, the process will be reversible when $\Delta G_{sys} = 0$ but $\Delta S_{sys} > 0$.

(Answer)

T

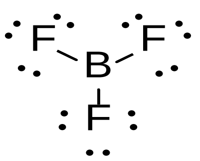
(e) In the phase diagram, both the negative and positive slope for solid/liquid line is possible.

(Answer)

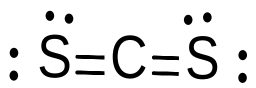
T

2. (total 10 pts, each 2.5 pts) **(Chapter 6-52)** Draw a Lewis electron dot diagram for each of the following molecules and ions. Formulate the hybridization for the central atom in each case and give the molecular geometry. **(structure 0.5 pt / Geometry 1 pt / Hybridization 1pt)**

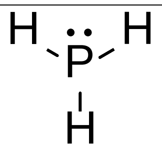
(a) BF_3

	SN of B : 3
	Formulate the hybridization of B : sp^2 hybridized
Lewis structure	Molecular geometry : trigonal-planar

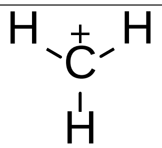
(b) CS_2

	SN of C : 2
	Formulate the hybridization of B : sp hybridized
Lewis structure	Molecular geometry : Linear

(c) PH_3

	SN of P : 4
	Formulate the hybridization of B : sp^3 hybridized
Lewis structure	Molecular geometry : pyramidal**(Tetrahedral, 정사면체라고 작성한 경우 0.5 pt)**

(d) **CH_3^+**

	SN of C : 3
	Formulate the hybridization of B : sp^2 hybridized
Lewis structure	Molecular geometry : trigonal-planar

3. (total 10 pts) **(Chapter 10-37)** Carbon dioxide is liberated by the reaction of aqueous hydrochloric acid with calcium carbonate:

$$CaCO_3(s) + 2\ H^+(aq) \ \ -> Ca^{2+}(aq) + CO_2(g) + H_2O(\ell)$$

A volume of 722 mL CO_2(g) is collected over water at 20 ℃ and a total pressure of 0.9963 atm. At this temperature, water has a vapor pressure of 0.0231 atm. Calculate the mass of calcium carbonate that has reacted, assuming no losses of carbon dioxide.

(Answer)

P_{CO_2} = P_{total} – P_{water} = 0.9963 atm – 0.0231 atm = 0.9732 atm (5 pts)

$$n_{CO_2} = \frac{P_{CO_2}V_{mixture}}{RT} = \frac{(0.9732\ \ atm)(0.722\ \ L)}{(0.08206\ \ L\ \ atm\ \ mol^{-1}K^{-1})(293.15K)}$$ **= 0.0292 mol CO_2**

$m_{CaCO_3} = 0.0292\ mol\ CO_2\ X\ \left(\frac{1\ mol\ CaCO_3}{1\ mol\ CO_2}\right)\left(\frac{100.09\ g\ CaCO_3}{1\ mol\ CaCO_3}\right)$ **= 2.92 $CaCO_3$ (5 pts)**

$(n_{CO_2} \rightarrow m_{CaCO_3})$ **calculation mistake -1 pt.**

4. (total 10 pts) (Chapter 13-65) The normal boiling point of liquid ammonia is 240 K; the enthalpy of vaporization at that temperature is 23.4 kJ mol^{-1}. The heat capacity of gaseous ammonia at constant pressure is 38 J mol^{-1} K^{-1}.

(a) [4 pts] Calculate q, w, ΔH, and ΔU for the following change in state:

$$2.00\ \text{mol}\ NH_3\ (l, 1\ atm, 240\ K) \longrightarrow 2.00\ mol\ NH_3\ (g, 1\ atm, 298\ K)$$

Assume that the gas behaves ideally and that the volume occupied by the liquid is negligible.

(Answer)

q	w	ΔH	ΔU
$51.2 \times 10^3\ J$	$-4.96 \times 10^3\ J$	$51.2 \times 10^3\ J$	$46.2\ J$

Each 1pts

The ΔH for the change equals the sum of the ΔH's of two steps: vaporization of NH_3 at 240K and heating of the vapor from 240 K to 298K. It is

$$\Delta H = \Delta H_1 + \Delta H_2 = n\Delta H_{vap} + nC_p\Delta T$$

$$= 2.00\ \text{mol}\ (23.4 \times 10^3 J\ mol^{-1}) + 2.00\ mol\left(\frac{38\ J}{K\ mol}\right)(298 - 240)K$$

$$= 51.2 \times 10^3\ J$$

The q for the two-stage change depends on the path and both changes occur at constant pressure. Therefore q equals the preceding ΔH, that is, $q = 51.2 \times 10^3\ J$.

The change absorbs some pressure-volume work. To this compute this work,

$$w = -P\Delta V = -P(V_2 - V_1) = -P(V_{gas} - V_{liq})$$

The V_{liq} in this equation is the volume of 2.00 mol of liquid ammonia at the starting temperature. According to the problem, this volume can be neglected in comparison to V_{gas}, the volume of the gas at the final temperature. Therefore

$$w = -PV_{gas} = -P\frac{nRT}{P} = -(2.00\ mol)(8.3145\ J\ K^{-1}\ mol^{-1})(298\ K) = -4.96 \times 10^3\ J$$

By the first law of thermodynamics

$$\Delta U = q + w = (51.2 \times 10^3\ J) + (-4.96 \times 10^3\ J) = 46.2\ J$$

(b) [6 pts] Calculate the entropy of vaporization of NH_3 at 240 K

(Answer)

$$\Delta S = \frac{\Delta H_{vap}}{T} = \frac{23.4 \times 10^3\ J\ mol^{-1}}{240\ K} = \mathbf{97.5\ J\ K^{-1} mol^{-1}}$$

This is also the standard molar entropy of the transition at 240 K.

No partial point (unit calculation error, -1 point)

5. (total 10 pts) (Chapter 14-26) A certain amount of NOBr(g) is sealed in a flask, and the temperature is raised to 350K. The following equilibrium is established:

$$NOBr(g) \rightleftarrows NO(g) + \frac{1}{2}\ Br_2\ (g)$$

The total pressure in the flask when equilibrium is reached at this temperature of 0.675 atm, and the vapor density is 2.219 g L^{-1}. Molecular weight of NOBr is 109.91 g mol^{-1}.

(a) [6 pts] Calculate the partial pressure of each species at equilibrium.

(Answer)

$\boldsymbol{P_{NOBr}}$	$\boldsymbol{P_{NO}}$	$\boldsymbol{P_{Br_2}}$
0.389 atm	**0.190 atm**	**0.0952 atm**

Each 2pts, no partial point

The vapor density of the contents of the flask cannot change in this gas-phase reaction. Before any of the NOBr (g) has a chance to react,

$$P_{NOBr} = \left(\frac{n}{V}\right) RT = \left(2.219\ g\ L^{-1} \times \frac{1\ mol}{109.91\ g}\right)(0.08206\ L\ atm\ mol^{-1}K^{-1})(350\ K) = 0.5698 atm$$

Setting up a three-line table:

	$NOBr(g)$	$\rightleftarrows NO(g)$	$+ \frac{1}{2}\ Br_2\ (g)$
Initial partial pressure (atm)	0.5798	0.0	0.0
Change in partial pressure (atm)	$-x$	$+x$	$+\frac{1}{2}x$
Equilibrium partial pressure (atm)	0.5789$-x$	x	$\frac{1}{2}x$

The final pressure in the flask, the sum of the three partial pressure, is 0.675 atm. It follows that

$$P_{NOBr} + P_{NO} + P_{Br_2} = (0.5698 - x) + x + \frac{1}{2}x = 0.675$$

The value of x is 0.1904 atm, so the three partial pressures are 0.389 atm, 0.190 atm, and 0.0952 atm at equilibrium.

(b) [4 pts] Calculate the equilibrium constant at this temperature.

(Answer)

Substituting the equilibrium partial pressures into the proper expression gives the numerical equilibrium constant

$$\frac{P_{Br_2}^{\frac{1}{2}} P_{NO}}{P_{NOBr}} = \frac{(0.0952)^{\frac{1}{2}}(0.190)}{0.390} = \mathbf{0.15} = K_{350}$$

No partial point (In case of calculation error, 50% deduction)

6. (total 10 pts) Consider BO (boron-oxygen) and the effect of adding an electron, $\mathrm{BO} + \mathrm{e}^- \rightarrow \mathrm{BO}^-$.

(a) [5 pts] Write the molecular electronic configurations for BO and BO^-.

(Answer)

$$\mathrm{BO}: (\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^1$$

$$\mathrm{BO}^-: (\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^2$$

(2.5 pts for each electronic configuration)

(b) [5 pts] Assess the effect of adding an electron on the bond length and strength of the molecule BO and explain why.

(Answer)

Bond order of BO : $1/2(7-2) = 5/2$

Bond order of BO^- : $1/2(8-2) = 3$

Bond order increased from 5/2 to 3, resulting in the shorter bond length and the stronger bond.

(2 pts for answers without any explanation)

(5 pts for answers with correct reasoning including the bond order calculation)

7. (total 10 pts) (Chapter 9-40) The partial pressure of oxygen in a mixture of oxygen and hydrogen is 0.200 atm, and that of hydrogen is 0.800 atm.

(R = 0.08206 L atm mol^{-1} K^{-1}, Molecular mass H_2O = 18.02 g mol^{-1})

(a) [3 pts] How many molecules of oxygen are in a 1.500-L container of this mixture at 40°C? (The unit uses the mole)

(Answer)

$$n_{O_2} = \frac{P_{O_2}V}{RT} = \frac{(0.200\ atm)(1.500\ L)}{(0.08206\ L\ atm\ mol^{-1}\ K^{-1})(313.15K)} = 1.167 * 10^{-2}\ mol$$ (or 7.03 x 10^{21})

+3 pts for right answer(unit, power error -1 pt)

(b) [3 pts] How many molecules of hydrogen are in a 1.500-L container of this mixture at 40°C? (The unit uses the mole)

(Answer)

$$n_{H_2} = \frac{P_{H_2}V}{RT} = \frac{(0.800\ atm)(1.500\ L)}{(0.08206\ L\ atm\ mol^{-1}\ K^{-1})(313.15K)} = 4.670 * 10^{-2}\ mol$$ or (2.81 x 10^{21})

+3 pts for right answer(unit error -1 pt)

(c) [4 pts] If a spark is introduced into the container, how many grams of water will be produced?

$$2\ H_2\ (g) + O_2\ (g) \rightarrow 2\ H_2O(\ell)$$

(Answer)

Oxygen is the limiting reactant

$$n_{water} = \left(\frac{2\ mol\ H_2O}{1\ mol\ O_2}\right)(1.167 * 10^{-2}\ mol\ O_2) = 2.335 * 10^{-2}\ mol\ H_2O$$

$$m_{water} = (2.335 * 10^{-2}\ mol\ H_2O)(18.02\ g\ mol^{-1}) = 0.421\ g\ H_2O$$

+4 pts for right answer(unit error -1 pt)

8. (total 10 pts) The combustion of nitromethane is used as a fuel, and the reaction is as follow:

$$CH_3NO_2(l) + O_2\ (g) \rightarrow CO_2\ (g) + \ N_2\ (g) + H_2O\ (g)\ \ \dots\dots\dots\dots\dots(unbalanced)$$

(a) [6 pts] Calculate the standard enthalpy change (ΔH°) for nitromethane using the following data table. The ΔH°_{rxn} for the balanced reaction is -1288.5 kJ.

Substance	ΔH°_f (25°C) kJ/mol	S°(25°C) J/K·mol	ΔG°_f (25°C) kJ/mol	C_p (25°C) J/K·mol
$CO_2\ (g)$	-393.51	213.63	-394.36	37.11
$H_2O\ (g)$	-241.82	188.72	-228.59	35.58

(Answer)

The balanced equation is

$\boldsymbol{4CH_3NO_2(l) + 3O_2\ (g) \rightarrow 4CO_2\ (g) +\ \ 2N_2\ \ (g) + 6H_2O\ \ (g)}$............**2pts**

Because of the most stable form of chemical elements such as O_2, N_2, and graphite is assigned as **zero enthalpy,** the standard enthalpy change of the total reaction is……….**2pts**

$$\Delta H^\circ_{rxn} = -1288.5\ \ kJ = \left[4mol\left(-\frac{393.51kJ}{mol}\right) + 6mol\left(-\frac{241.82kJ}{mol}\right)\right] - \left[4mol\left(\Delta H^\circ_{f,CH_3NO_2}\right)\right]$$

Solving, $\Delta H^\circ_{f,CH_3NO_2} = -434.12\ \ kJ/mol$………**2pts**

Balanced equation 2pts

If you know that oxygen and nitrogen enthalpy is assigned as zero, 2pts

Right answer 2pts

(b) [4 pts] A 25.0L flask filled with nitromethane and O_2, is heated to 100℃. After the reaction is complete, the total pressure of all the gas inside the flask is 125 atm at the temperature. If the mole fraction of nitrogen ($x_{nitrogen}$) is 0.2 after the reaction is complete, what mass of nitrogen was produced?

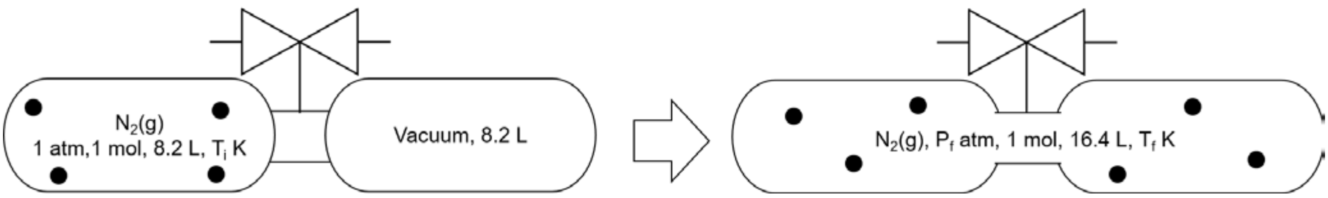
(Answer)

$$P_{N_2} = P_{total} \times x_{N_2} = 1.25atm \times 0.2 =\ \ \underline{\mathbf{25\ \ atm\ \ldots\ldots\ldots 2pts}}$$

$$n_{N_2} = \frac{25\ \ atm\ \ \times 25.0\ \ L}{\frac{0.08206\ \ L\ \ atm}{K\ \ mol} \times 373K} = 20.4\ \ mol\ \ N_2$$

$$20.4\ \ mol\ \ N_2 \times \frac{28.02\ \ g\ \ N_2}{1\ \ mol\ \ N_2} = \underline{\mathbf{572\ \ g\ \ N_2\ \ \ldots\ldots\ldots\ 2pts}}$$

9. (total 10 pts) Consider the free expansion of 1 mol nitrogen gas(T = T_i) from 8.2 L to 16.4 L in an isolated container system. Assume that N_2 gas behaves like an ideal gas.



(a) [3 pts] Calculate T_i, T_f, P_f.

(Answer)

Ti = P_iV_i/nR = (1 atm)(8.2 L)/(1 mol)(0.082 atm L/mol K) = 100 K

Since this system is isolated, there is no heat transfer; q = 0 -

Also, there is no work since there is no pressure(vacuum); w = 0

$\Delta U = q + w = 0 = nc_v\Delta T$

No temperature change, so $T_f = T_i$

No internal energy change, so $P_iV_i = P_fV_f$, **$P_f = Pi(V_i/V_f)$ = 1 atm (8.2 L/16.4 L) = 0.5 atm**

each +1 point for T_i, T_f, and P_f

(b) [4 pts] Calculate the q, w, ΔH, and ΔU for this process.

(Answer)

q = 0, w = 0, ΔU = q + w = 0, ΔH = ΔU + Δ(PV) = 0

each +1 point for q, w, ΔU, and ΔH

(c) [3 pts] Distinguish and explain why whether this process is reversible or irreversible, and spontaneous or nonspontaneous. (Hint: $\Delta S = \mathrm{nR}\ln\frac{V_f}{V_i}$ in free expansion)

(Answer)

$\Delta S = \mathrm{nR}\ln\frac{V_f}{V_i}$ = nR ln 2 = (1 mol)(8.314J/mol K)(0.6931) = 5.76 J/K > 0 -> **Spontaneous, Irreversible**

+2 point

or ΔG = ΔH – TΔS = 0 – (100 K)(5.76 J/K) = -576 J ≠ 0 -> **Spontaneous, Irreversible**

+2 point

+1 for right explanation

10. (total 10 pts) Consider the following chemical reactions and their equilibrium constants.

Eq 1. A(g) → B(g) + C(g): $K_1 = 1/4$

Eq 2. B(g) → D(g) + C(g): $K_2 = 3$

Eq 3. A(g) → D(g) + 2C(g): $K_3 = ?$

At an equilibrium, suppose that the concentrations of the species A and B are [A] = 4 and [B] = 1.

(a) [3 pts] Calculate the concentrations of the other species at the equilibrium and K_3.

(Answer)

From Eq 1, K_1 = [B][C]/[A] = [C]/4 = 1/4.

Therefore, [C] = 1 ------ (1)

+1 points

From Eq 2, K_2 = [D][C]/[B] = [D] = 3 -------- (2)

[A] = 4, [B] = [C] = 1, [D] = 3

+1 points

Eq 3 can be obtained by adding Eq 1 and Eq 2. Thus,

$K_3 = K_1 * K_2 = 3/4$

+1 points

(b) [4 pts] The concentration of the species B has been increased abruptly up to [B] = 2 under the constant volume and temperature. Guess whether the concentration of C is going to increase at the new equilibrium or not? Justify your answer.

(Answer)

Due to the Le Châtelier's principle, the reverse process of Eq 1 and the forward process of Eq 2 will be spontaneous.

+2 point

The former consumes C, whereas the latter produces C. The equilibrium constant of the reverse reaction of Eq 1 is larger than that of Eq 2. Hence, the former is favored, resulting in the reduction of [C].

+2 points

(c) [3 pts] Propose a way to quantitatively determine the concentration of C at the new equilibrium.

(Answer)

Let the reduction of [C] by the former and the latter –x and +y, respectively. Then, the concentration of each species at the new equilibrium will be as follows.

[A] = 4 + x, [B] = 2 - x – y, [C] = 1 – x + y, [D] = 3 + y.

+1 point

Since equilibrium constants do not change under the constant temperature, the three equations should hold the following relations.

$K_1 = (2 - x - y)(1 - x + y) / (4 + x) = 1/4$

$K_2 = (3 + y)(1 - x + y) / (2 - x - y) = 3$

$K_3 = (3 + y)(1 - x + y)^2 / (4 + x) = 3/4$

+1 point

To simplify the above equations, let $x + y = 2a$ and $x - y = 2b$. As a result,

$K_1 = (2-2a)(1-2b)/(4+a+b) = 1/4$

It gives

$a = (4-16b)/(9-16b)$ ------- (1)

$K_2 = (3+a+b)(1-2b)/(2-2a) = 3$

$2b^2 + 5b = 7a - 2ab – 3$ -------- (2)

Using eqs (1) and (2), one can determine the values of a and b, subsequently x and y, leading to the final concentration. For example, eq (1) can be substituted in eq (2). Or by rewriting eq (2) as

$2b_{i+1}+5b_{i+1} = 7a -2ab_i$ ------ (3)

Eqs (1) and (3) can be iteratively solved.

+1 points