2022 Spring Semester Midterm Examination
For General Chemistry I

Date: April 20 (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	/12	**6**	/10	**/100**
2	/6	**7**	/12	
3	/12	**8**	/12	
4	/10	**9**	/10	
5	/6	**10**	/10	

** This paper consists of 20 sheets with 10 problems (***page 18 - 19***: Equation, constants & periodic table, ***page 20***: 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.
(채점 답안지 분배 및 이의신청 일정)

1. Period, Location and Procedure

1-1) For students who took the off-line Examination

0 Return and Claim Period: April 25 (Mon, 19:00 ~ 21:00, 2 hrs)

The claim is permitted only on this period. Keep that in mind!

0 Location: Each designated room of Creative Learning Bldg. (E11)

Class	Room(E11)	Class	Room(E11)
A	101	D	301
B	102	E	302
C	103	F	303

0 Procedure

Rule 1: Students cannot bring their writing tools into the rooms (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, write them on the claim form and attach it to the top of the exam paper with a stapler. Give them to your TA.

WARNING!!
If you deliberately alter any original answers or insert something on your marked paper to achieve a better grade, you will get a F grade for this course. Or if you don't keep the rules above, we will regard it as a kind of cheating and give you 0 point. So please don't cheat.

1-2) For Students who took the online examination

0 **Claim Period:** April 25 (Mon, 19:00 ~ 21:00, 2 hrs)
The claim is permitted only on this period. Keep that in mind!
0 Location: Each class of Turnitin site
0 Procedure
If you have any claims on it, email them (Question# and reasons) to ***each TA in charge of the # of each question***. *The TA name and email addresses will be announced on the General Chemistry Website*.

2. Final Confirmation

1) Period: ***April 28(Thu) ~ 29(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 12 pts)

In ionic compounds, the potential energy, $V(R_{12})$, is expressed as a function of the distance between the ions (R_{12}), choosing as zero the potential energy of the neutral atoms when they are infinitely far apart.

$$V(R_{12}) = \underbrace{Ae^{-\alpha R_{12}}}_{(1)} - \underbrace{B\left(\frac{(e)(-e)}{R_{12}}\right)}_{(2)} + \underbrace{\Delta E_{\infty}}_{(3)}$$

(a) What do the three terms of the equation ((1), (2), and (3)) represent? (3 pts)

(Answer) 1 pt each 각 항의 설명이 맞을 경우 1점

(1) repulsion between the ions as they get very close together

(2) attractive Coulomb potential

(3) energy required to create the ions from their respective neutral atoms

: 반발, 인력, 무한에서의 값, IE-EA등 핵심 키워드가 있을 경우 점수 부여. 단, 입자를 특정하였는데 틀릴 경우, 설명이 부족하여 다른 의미로 해석될 수 있는 경우 점수 부여 안함.

(b) Consider the ionic compound KF. Given that the first ionization energy of potassium is 419 kJ/mol and electron affinity of fluorine is 328 kJ/mol, calculate ΔE_{∞}. (2 pts)

(Answer)

$$\Delta E_{\infty} = IE_1(K) - EA(F) = +91\ kJ/mol$$

91 kcal/mol 이외의 답은 0점. 단위 미기재시 2점 중 1점 감점

(c) Calculate the energy changes (ΔE) for the following pairs of reactions:

$$K(g) + F(g) \rightarrow K^{+}(g) + F^{-}(g)$$

$$K(g) + F(g) \rightarrow K^{-}(g) + F^{+}(g)$$

Explain why $K^{+}F^{-}$ forms in preference to $K^{-}F^{+}$.

The first ionization energy of fluorine is 1681 kJ/mol and the electron affinity of potassium is 48 kJ/mol. (3 pts)

(Answer)

The 1st reaction involves 419-328 = 91 kJ/mol, while the 2nd reaction involves 1681-48 = 1633 kJ/mol. The 1st reaction is energetically favored prior to the formation of the ionic compound.

V

91kJ/mol, 1633kJ/mol 각각 1점. 부분점수 없음. 단위 없을시 총 -0.5점 감점.(중복없음)

첫번째 값은 (b)의 문제와 동일하여 단순 생략한 학생이 많으므로, 학생이 반응식과 (b)가 동일함을 이해하는 것으로 보이면 (b)의 값을 차용.(ΔE∞ 기호, IE-EA 식 사용 등)/ 따로 어떤 값을 적은경우, 해당값 사

용.

1점: K+F-가 왜 더 잘 생기는지 원자단위 혹은 반응식 등을 설명하면 점수부여.

ex) K+F- 가 K-F+ 에너지 변화 비교, 훨씬 stable함 언급, F와 K의 큰 IE차이 를 통해 나타난 에너지 변화 차이 . 옥텟룰, 전기음성도 등으로 인한 K+와 F-의 안정성 차이 등등

(d) The estimated energy of dissociation (ΔE_d) to neutral atoms for KF, which has a bond length of 2.17 Å, is 549 kJ/mol. From the given bond length and energy values, draw the potential energy curve of the ions K^+ and F^- as a function of their internuclear separation R_{12}. (4 pts)

(Answer)

그래프 모양: 1점 (포물선 등 감점, y축,x축 평행이동 상관없음)

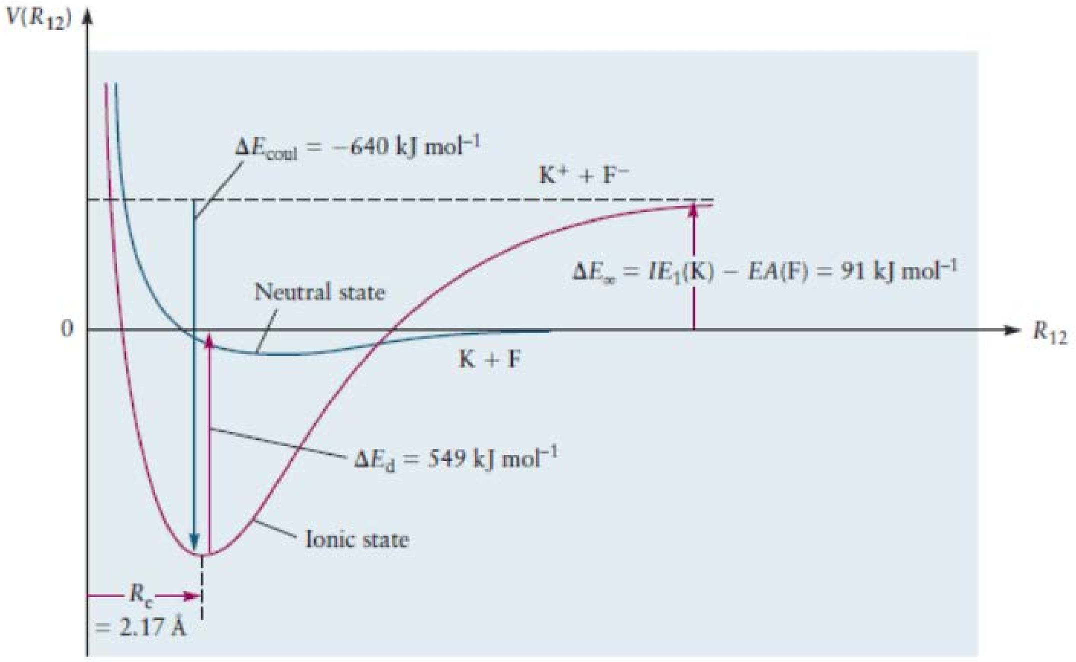
Re= 2.17A 위치 및 값 지정 1점.

Ed = 549kJ/mol 값 및 지정 1점.

ΔE∞ 정확한 값지정 필요 없음. x축 밑으로 그래프가 내려가는 경우, 혹은 그래프가 계속 발산하는 경우 감점 1점. 그외에 1점 부여.

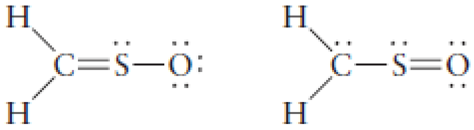
축 및 단위 없을 시, 통합 총 -0.5 감점.

Figure 3.13

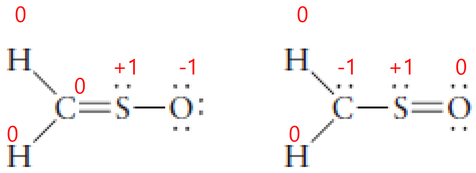


2. (total 6 pts)

Two possible Lewis diagrams for sulfine (H_2CSO) are



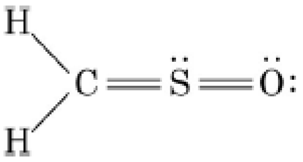
(a) Indicate the formal charges on all atoms of these two Lewis diagrams. (4 pts)



각 분자의 원소의 formal charge 하나당 +0.5점 (각 분자의 H는 두 개 합쳐서 0.5점)

형식 전하가 0인 경우에도 표시하지 않으면 감점

(b) Draw a Lewis diagram, where all the atoms in sulfine have formal charges of zero. (2 pts)



2 pts

공유 전자쌍 모두 잘 표시했으면 +1점

비공유 전자쌍 모두 잘 표시했으면 +1점

Sulfine 외 다른 분자 구조 : 0점

3. (total 12 pts)

An electron is confined to a 1.20 nm one-dimensional box. Suppose this electron undergoes transitions among all possible states, and several visible spectral lines are observed as a result of these transitions. Visible light has the wavelength between 400 nm and 700 nm, and the energy levels of the electron in a box is $E_n = \frac{n^2 h^2}{8mL^2}$

For (a) and (b), determine whether the emitted light by the following transition is in the visible spectrum.

(a) n=2 to n=1 (3 pts)

$$E_2 - E_1 = (2^2 - 1^2)\cdot\frac{h^2}{8mL^2} = \frac{3h^2}{8mL^2} = \frac{3\times(6.626\times10^{-34} J\, s^{-1})^2}{8\times(9.109\times10^{-31}\, kg)\times(1.20\times10^{-9}\, m)^2}$$

$$= 1.26\times10^{-19} J = h\frac{c}{\lambda}$$

$$\therefore \lambda = \frac{hc}{E_2 - E_1} = \frac{(6.626\times10^{-34} J\, s^{-1})\times(2.998\times10^{8}\, m\, s^{-1})}{1.26\times10^{-19} J} = 1580\, nm$$

2 pts

It is above 700 nm, so it does NOT result in the visible spectrum.

1 pts

(b) n=3 to n=1 (3 pts)

$$E_3 - E_1 = (3^2 - 1^2)\cdot\frac{h^2}{8mL^2} = \frac{8h^2}{8mL^2} = \frac{8\times(6.626\times10^{-34} J\, s^{-1})^2}{8\times(9.109\times10^{-31}\, kg)\times(1.20\times10^{-9}\, m)^2}$$

$$= 3.34\times10^{-19} J = h\frac{c}{\lambda}$$

$$\lambda = \frac{hc}{E_2 - E_1} = \frac{(6.626\times10^{-34} J\, s^{-1})\times(2.998\times10^{8}\, m\, s^{-1})}{3.34\times10^{-19} J} = 595\, nm$$

2 pts

It is within the 400 nm – 700 nm region, so it DOES result in the visible spectrum.

1 pts

단위없으면 1점 감점, 파장이 아닌 E 기준으로 풀어도 3점

(c) How many visible spectral lines can we observe? (6 pts)

For any transition from n_i to n_f where i>f,

$$\lambda = \frac{hc}{\Delta E} = hc \times \frac{8mL^2}{(n_i^2 - n_f^2)h^2} = \frac{8mcL^2}{(n_i^2 - n_f^2)h}$$

$$= \frac{8 \times (9.109 \times 10^{-31}\ kg) \times (2.998 \times 10^8\ m\ s^{-1}) \times (1.20 \times 10^{-9}\ m)^2}{(n_i^2 - n_f^2) \times (6.626 \times 10^{-34} J\ s^{-1})}$$

$$= \frac{4747\ nm}{n_i^2 - n_f^2}$$

In order to fall in the visible region:

$$400\ nm < \frac{4747\ nm}{n_i^2 - n_f^2} < 700\ nm$$

3 pts

$$6.78 < n_i^2 - n_f^2 < 11.9$$

There are four transitions satisfying this condition: 3 to 1, 4 to 3, 5 to 4, and 6 to 5.

Therefore, four visible spectral lines must be observed.

3 pts

부등식 없이 일일이 계산하여 맞으면 6점, 풀이과정 없이 답만 맞으면 3점

4. (total 10 pts)

(a) Take note that ionization energies for the 1s electrons of the second-row atoms are

Atom	**Energy(kJ/mol)**	**Atom**	**Energy(kJ/mol)**	**Atom**	**Energy(kJ/mol)**	**Atom**	**Energy(kJ/mol)**
Li	4820	Be	10,600	B	18,300	C	27,000
N	38,600	O	51,000	F	66,600		

Now suppose that a certain substance is bombarded by X rays having a wavelength of 0.989 nm. If photoelectrons with kinetic energies of 94,000 kJ/mol and 69,900 kJ/mol are ejected from the material, which of the elements listed above must be present in the sample? (6 pts)

(Sol)

$E = h\upsilon = \frac{hc}{\lambda}$, part of which plays for ionization(I) while the rest goes into the kinetic energy of the ejected photoelectron ($\frac{1}{2}mv^2$).

$$E = I + \frac{1}{2}mv^2$$

$$E = h\upsilon = \frac{(6.63 \times 10^{-34} Js)(3.00 \times 10^8 s^{-1})}{0.989 \times 10^{-9} m} \times \frac{6.02 \times 10^{23}}{mol} = 1.21 \times 10^5 kJ/mol$$

For 94,000 kJ/mol

$$E = I - \frac{1}{2}mv^2 = (1.21 - 0.94) \times 10^5 kJ/mol = 2.7 \times 10^4 kJ/mol$$

Attribute to carbon atom

3 pts

For 69,900 kJ/mol

$$E = I - \frac{1}{2}mv^2 = (1.21 - 0.699) \times 10^5 kJ/mol = 5.11 \times 10^4 kJ/mol$$

Attribute to oxygen atom

3 pts

(b) The energy needed to remove one electron from a gaseous potassium atom is only about two-thirds as much as that needed to remove one electron from a gaseous calcium atom, yet nearly three times as much energy as that needed to remove one electron from K^+ as from Ca^+. 1) What explanation can you give for this difference? 2) And compare the ionization energy of Ca^+ and that of neutral K? (4 pts)

Answer

(2 pts each)

1) For both K and Ca, the outer electrons are in the 4s shell, outside of the Ar core. K has the lower ionization energy because of its lower nuclear charge. The second 4s electron in Ca only partially shields the first. K^+ is isoelectronic with Ar; Ca^+ is isoelectronic with K. Thus, the comparison of the ionization energies of K^+ and Ca^+ echoes that of Ar and K. Ca^+ has an appreciably lower ionization energy.

Comparing K/Ca with effective nucelar charge: 1 point

Compring K+/Ca+ by mentioning the stable state of K+: 1 point

2) In comparing K with Ca^+ (i.e., the first ionization energy of K with the second of Ca), one is comparing isoelectronic species. The one with the higher nuclear charge (Ca^+) has the higher ionization energy.

5. (total 6 pts)

Consider a following orbital wave function of a hydrogen atom:

$$\psi = \frac{1}{81\sqrt{3\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}(27 - 18\sigma + 2\sigma^2)e^{-\frac{\sigma}{3}}$$

(a) Determine the number of radial nodes and angular nodes for this orbital. (2 pts)

From the term $(27 - 18 + 2\sigma^2)$, we can figure out that there are two radial nodes.

Meanwhile, because there are no terms of θ and ϕ, there is no angular node.

(Radial node, angular node 각각 1점)

(b) Determine the principal quantum number of this orbital. (2 pts)

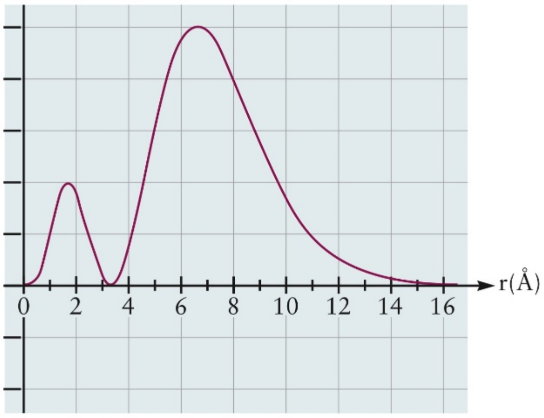
Since there is no angular node, l = 0

Number of radial nodes = 2

Therefore, 2 = n-l-1=n-0-1, n=3

n=3: 2점 (l, m 무시)

(c) Is the following graph a correct representation of this orbital's radial probability density? Explain. (2 pts)



(Answer)

n=3, l=0: The given orbital in the problem is a 3s molecule with two radial nodes.

However, this graph shows only one radial node.

Therefore, this is NOT a correct representation of this orbital.

그래프가 틀렸다는 것을 명시하고 올바르게 설명한 경우: 2점

그래프가 틀렸다는 것을 명시하고 올바르게 설명하였지만 (a)에서 radial node가 1개라고 명시한 경우: 1점

그래프가 틀렸다는 것을 명시하였지만 설명이 틀린 경우: 1점

그래프가 맞다고 명시한 경우: 0점

6. (total 10 pts)

Use valence bond (VB) theory to predict the hybridization in formaldehyde and allene. Sketch the hybrid atomic orbitals depicting their overlaps and σ and π-bonding.

a) formaldehyde $H_2C{=}O$ (5 pts)

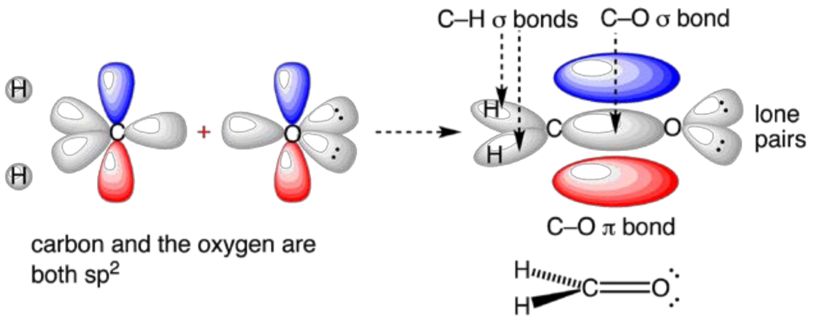
b) allene $H_2C{=}C{=}CH_2$ (5 pts)

(Sol)

a) C atom is sp^2 hybridized, as is the O atom.

These trigonal planar sp^2 orbitals σ bonded with 1s orbital of H atom and 2p orbital of O atom.

Unhybridized 2p orbital of C atom and O atom form π bond which is orthogonal to σ bond.

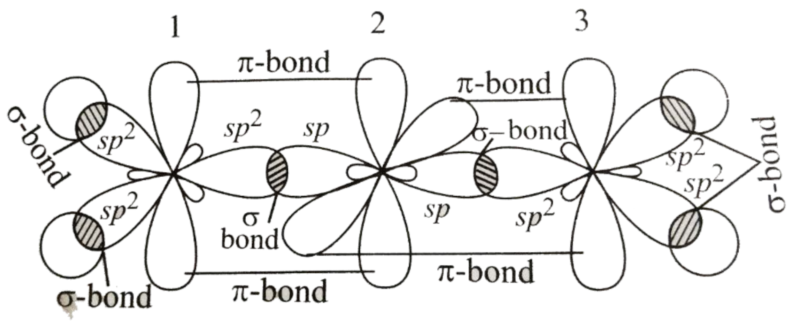


C : sp2 (1점) O : sp2 (1점) ->명확하게 표시하지 않았을 경우 0점, sigma bond, pi bond를 orbital에 직접 표시하여 그렸을 경우 (각 1점 -> 틀리게 적거나, 빠진 것이 있다면 점수 부여x), atomic orbital을 제대로 그렸을 경우 1점 -> lone pair 그리지 않았으면 0점

b) The central C atom forms one π bond on each side. These π bonds are orthogonal to σ bond.

The central C atom must be sp hybridized. The terminal C atoms are sp^2 hybridized.

These sp^2 orbitals are σ bonded with 1s orbitals of H atoms and sp hybrid orbital of central C atom.



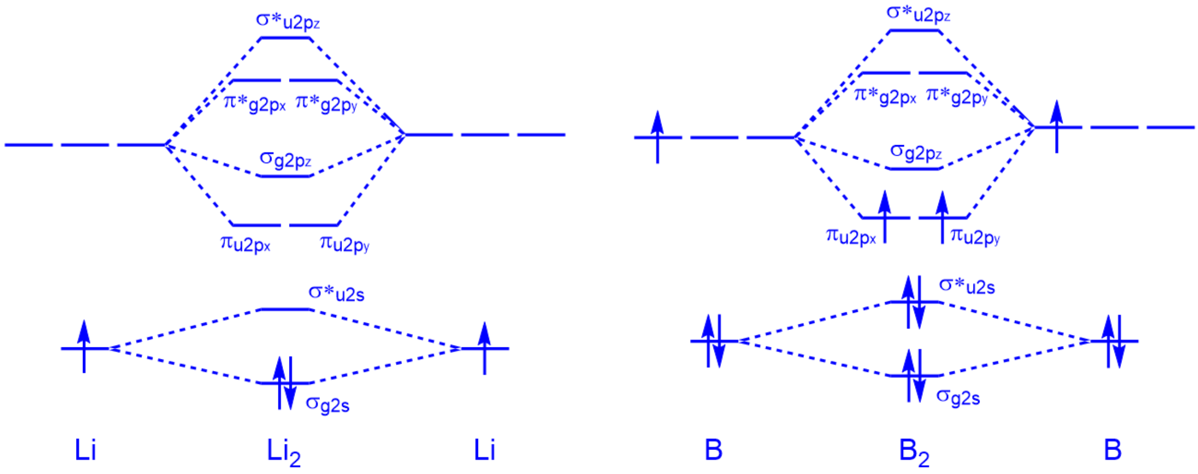
(C center sp (1점), C side sp2 (1점) -> 명확하게 표시하지 않았을 경우 0점, sigma bond, pi bond를 orbital에 직접 표시하여 그렸을 경우 (각 1점 -> 틀리게 적거나, 빠진 것이 있다면 점수 부여x), atomic orbital을 제대로 그렸을 경우 1점

7. (total 12 pts)

Molecular orbital diagram provides useful insights on the molecular properties. Answer the following questions.

(a) Construct LCAO-MO correlation diagrams (consider only 2s and 2p) with assigned electrons for Li_2 and B_2. (4 pts)

(Answer)



(b) Calculate bond order and assign magnetic properties (diamagnetic or paramagnetic) of Li_2 and B_2. (4 pts)

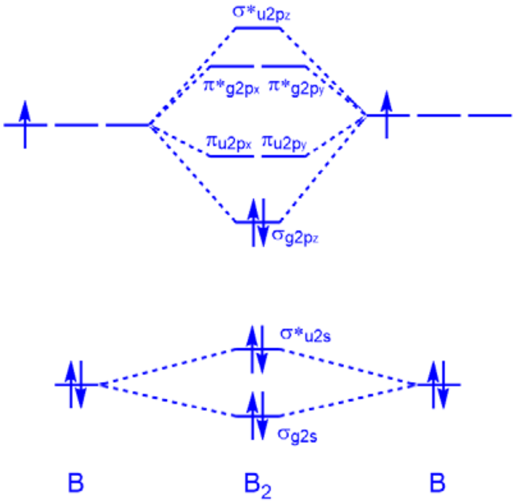
(Answer) (each 1 pt)

Li_2 : bond order 1; diamagnetic

B_2 : bond order 1; paramagnetic

(c) Suppose the energy gap between 2s and 2p of boron is as great as fluorine (F). Draw the MO diagram and predict the magnetic property of B_2 with this assumption. Briefly explain your answer. (4 pts)

As the energy gap between s and p orbital greater, the mixing becomes ignorable and σ_{2s} will lower-lying than π_{2p}. The electron configuration of B_2 will be change as shown below.



(3 pts)

diamagnetic.

(1 pts)

8. (total 12 pts)

The Haber-Bosch process converts molecular nitrogen (N_2) and hydrogen (H_2) into gaseous ammonia (NH_3) at elevated temperature and pressure. Following is a 100 mL Schlenk flask that is used to run the reaction. An iron-based solid-state catalyst was firstly added to the flask. Air in the tube was evacuated under vacuum, and the flask was subsequently charged and sealed with 1000 torr of N_2 and 1000 torr of H_2 at 27 °C. Assuming that the system follows the ideal gas law and the solid-state catalyst does not have appreciable volume.

(a) Calculate the molar fraction of N_2 before any reaction happens. (2 pts)

(Answer)

$\chi_{N2} = P_{N2} / (P_{N2}+P_{H2}) = 1000\ \text{torr} / (1000+1000)\ \text{torr}) = 0.5$

1/2, 0.5 제외 모두 오답처리

(b) Calculate how much N_2 is charged in the flask in gram before any reaction happens. (2 pts)

(Answer)

$$P_{N2}V = n_{N2}RT$$

$$\frac{1000\ torr}{760\ torr/atm}\cdot 0.100\ L = n\cdot(0.082\ atm\cdot L/mol\cdot K)\cdot 300\ K$$

$$\text{n} = 0.00534\ \text{mol} = 5.34\ \text{mmol}$$

$$m_{N2} = \text{Mw}\cdot\text{n} = (28.02\ \text{g/mol})(0.0534\ \text{mol}) = 0.150\ \text{g}$$

No partial point.

단위 감점 (b) -0.5, (c) -1

0.150g 내외 정답처리, 단 계산식/대입값 오류 존재 시 오답 처리

(c) By heating the mixture to 600 K, the desired reaction happened. After completion, the flask was cooled down to 27 °C, and the total pressure of the system was measured as 1000(→1500) torr. Calculate how much ammonia was generated in mole. (4 pts)

(Answer) 8c는 문제 오류로 인해 아래의 여러 답안을 인정합니다.

1) 위 문제는 말이 안된다.

2) 기존 답안 (1000torr 일 경우)

Applying $P_{total,after}V = n_{total,after}RT$, it gives $n_{total,after}$ = 5.34 mmol

Considering the balanced equation of the Haber-Bosch process,

N_2 + $3\ H_2$ -> $2\ NH_3$

Before | 5.34 mmol 5.34 mmol

Rxn | -x -3x +2x

After | (5.34-x) mmol (5.34-3x) mmol (2x) mmol

$n_{total} = n_{N2,after} + n_{H2,after} + n_{NH3,after} = (5.34 – x) + (5.34 – 3x) + 2x = (10.68 - 2x)$ mmol $= 5.34$

x= 5.34/2 mmol = 2.67 mmol

Thus, generated ammonia is 2x = 5.34 mmol = 0.00534 mol

No partial point.

3) 신규 답안 (1500torr 일 경우)

Applying $P_{total,after}V = n_{total,after}RT$, it gives $n_{total,after}$ = 8.02 mmol

Considering the balanced equation of the Haber-Bosch process,

N_2 + $3\ H_2$ -> $2\ NH_3$

Before | 5.34 mmol 5.34 mmol

Rxn | -x -3x +2x

After | (5.34-x) mmol (5.34-3x) mmol (2x) mmol

$n_{total} = n_{N2,after} + n_{H2,after} + n_{NH3,after} = (5.34 – x) + (5.34 – 3x) + 2x = (10.68 - 2x)$ mmol $= 8.02$

x= 2.67/2 mmol = 1.34 mmol

Thus, generated ammonia is 2x = 2.67 mmol = 0.00267 mol

No partial point.

몰 수, 압력 상관없이 계산 과정 및 값 맞으면 정답 처리

(d) Following the ideal gas law, the pressure exerted by 1 mole of carbon dioxide in a 536 mL vessel at 373 K is 57.1 atm. Using the van der Waals equation, calculate the pressure under the above condition. For CO_2, a = 3.592 atm L^2 mol^{-2} and b = 0.04267 L mol^{-1}. Do attractive or repulsive forces dominate in CO_2? (4 pts)

(Answer)

$$P = \frac{nRT}{V - nb} - a\frac{n^2}{V^2}$$
$$= \frac{(1\ mol)(0.08206\ L\ atm\ mol^{-1}\ K^{-1})(373\ K)}{0.536\ L - (1\ mol)(0.04267\ L\ mol^{-1})} - (3.592\ atm\ L^2\ mol^{-2})\frac{(1\ mol)^2}{(0.536\ L)^2}$$
$$= 49.5\ atm$$

3 pts

(Answer)

Attractive forces dominate in CO_2.

1 pts

압력 계산 및 값 맞는 경우, +3 attractive dominate 작성 시, +1

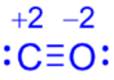
9. (total 10 pts)

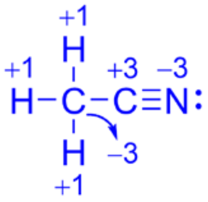
(a) Draw the Lewis structures and indicate oxidation numbers for all atoms of below molecules.

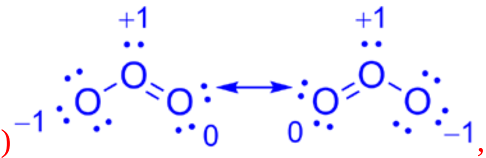
(i) carbon monoxide (CO, nonpolar), (ii) acetonitrile (CH_3CN; with a single C-C bond), (iii) ozone (O_3)

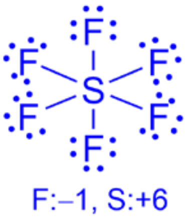
(iv) sulfur hexafluoride (SF_6) (6 pts)

Answer: 1.5 pt each

(a)


, (b)


, (c)


, (d)


각문제 1.5 점씩 산화수 0.5 점 루이스구조 1 점으로 분배했으며 루이스 구조는 전자를 표시하지 않으면 틀린 것으로 간주. (iii)의 경우 루이스 구조 맞아도 공명구조 없을 시 0.5 점 감점

(b) A table shown below shows van der Waals constants (a and b) for above molecules. Fill in the blank. (4 pts)

Molecular formula	a (atm*L^2*mol^{-2})	b (L*mol^{-1})
	1.47	0.040
	3.57	0.049
	7.86	0.088
	17.89	0.117

Molecular formula	a (atm*L^2*mol^{-2})	b (L*mol^{-1})
CO	1.472	0.0395
O_3	3.570	0.0487
SF_6	7.857	0.0879
CH_3CN	17.89	0.1169

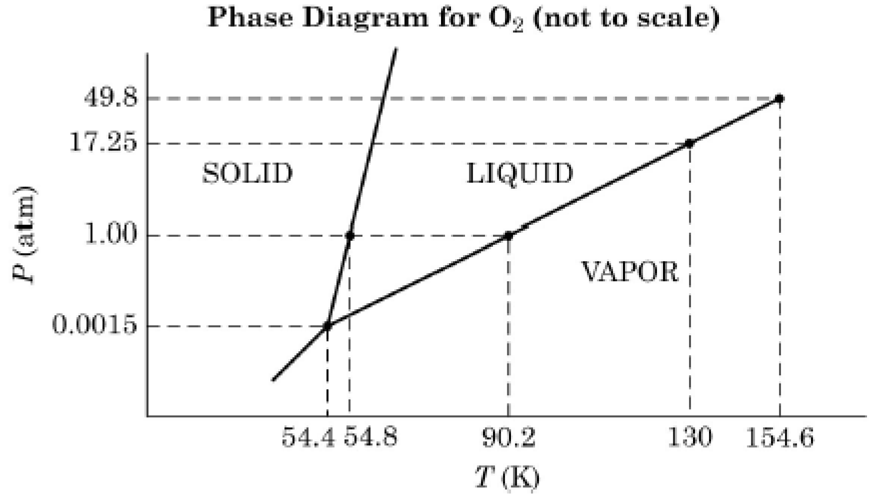
분자 하나당 1 점

10. (total 10 pts)

(a) Sketch the phase diagram of O_2 using the following information. Note that the density of O_2(l) is 1.31 g/cm^3, while density of O_2(s) is 1.36 g/cm^3. (indicate below four points in the diagram) (6 pts)

	P (atm)	T (K)
Triple point	0.0015	54.4
Critical point	49.8	154.6
Normal boiling point	1.000	90.2
Normal melting point	1.000	54.8

Answer) graph shape 1 pt, solid/liquid slope 1 pts, four points: each 1 pt



(b) In the planet Uranus, the atmospheric pressure is 1.2 atm with the average temperature of 55 K. Using the phase diagram, explain why Uranus does not have any oxygen in the atmosphere. (2 pts)

At 1.2 atm and 55 K, oxygen is either solid or liquid and cannot exist as a vapor state. Therefore, even if oxygen does exist in Uranus, it cannot exist in the atmosphere as vapor.

(c) O_2 at a pressure of 60 atm and a temperature of 54 K is heated to 200 K. How many and what phase transitions occur during the heating process? (2 pts)

One from solid to liquid (초임계유체로의 변화는 상전이 과정으로 보지 않음)

Physical Constants

Avogadro's number	$N_A = 6.02214179 \times 10^{23}\ \mathrm{mol}^{-1}$
Bohr radius	$a_0 = 0.52917720859$ Å $= 5.2917720859 \times 10^{-11}$ m
Boltzmann's constant	$K_B = 1.3806504 \times 10^{-23}\ \mathrm{J\ K}^{-1}$
Electronic charge	$e = 1.602176487 \times 10^{-19}$ C
Faraday constant	$F = 96485.3399\ \mathrm{C\ mol}^{-1}$
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	$\varepsilon_o = 8.854187817 \times 10^{-12}\ \mathrm{C}^{-2}\ \mathrm{J}^{-1}\ \mathrm{m}^{-1}$
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	$c = 2.99792458 \times 10^{8}\ \mathrm{m\ s}^{-1}$ (exactly)
Standard acceleration of terrestrial gravity	$g = 9.80665\ \mathrm{m\ s}^{-2}$ (exactly)
Universal gas constant	$R = 8.314472\ \mathrm{J\ mol}^{-1}\ \mathrm{K}^{-1}$ $= 0.0820574\ \mathrm{L\ atm\ mol}^{-1}\ \mathrm{K}^{-1}$

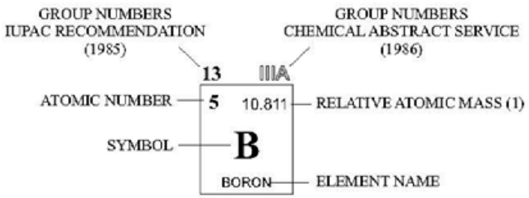
Values are taken from the 2006 CODATA recommended values,
as listed by the National Institute of Standards and Technology.

Conversion factors

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

PERIODIC TABLE OF THE ELEMENTS

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



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)

<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 bef*

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

2022 Spring Semester Final Examination
For General Chemistry I

Date: June 15 (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	/7	**7**	/12	**/100**
2	/8	**8**	/6	
3	/10	**9**	/10	
4	/12	**10**	/14	
5	/8	**11**	/6	
6	/7			

** This paper consists of 16 sheets with 11 problems (***page 14 - 15***: Equation, constants & periodic table, ***page 16***: 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.

(채점 답안지 분배 및 이의신청 일정)

1. Period, Location and Procedure

1-1) For students who took the off-line Examination

0 Return and Claim Period: ***June 17*** (Fri, 12:00 ~ 14:00, 2 hrs)

The claim is permitted only on this period. Keep that in mind!

0 Location: Each designated room of Creative Learning Bldg. (E11)

Class	Room(E11)	Class	Room(E11)
A	101	D	301
B	102	E	302
C	103	F	303

0 Procedure
Rule 1: Students cannot bring their writing tools into the rooms (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, write them on the claim form and attach it to the top of the exam paper with a stapler. Give them to your TA.

WARNING!!
If you deliberately alter any original answers or insert something on your marked paper to achieve a better grade, you will get a F grade for this course. Or if you don't keep the rules above, we will regard it as a kind of cheating and give you 0 point. So please don't cheat.

1-2) For Students who took the online examination

0 **Claim Period:** ***June 17*** (Fri, 12:00 ~ 14:00, 2 hrs)
The claim is permitted only on this period. Keep that in mind!
0 Location: Each class of Turnitin site
0 Procedure
If you have any claims on it, email them (Question# and reasons) to ***each TA in charge of the # of each question***.
The TA name and email addresses will be announced on the General Chemistry Website.

2. Final Confirmation

1) Period: ***June 18(Sat) ~ 19(Sun)***
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 7 pts)

(a) At 90 °C, the vapor pressure of toluene is 0.534 atm and the vapor pressure of benzene is 1.34 atm. Benzene (0.400 mol) is mixed with toluene (0.900 mol) to form an ideal solution. Compute the mole fraction of benzene in the vapor in equilibrium with this solution.

(b) Calculate the mole fraction of toluene in a mixture of benzene and toluene that boils at 90 °C under atmospheric pressure.

(c) Which liquid can be extracted by vapor from the original solution by conducting fractional distillation multiple times? Explain.

(answer)

(a) **3 pts**

$$\mathrm{P_{toluene}} = X_{toluene}P°_{toluene} = \left(\frac{0.900}{0.400 + 0.900}\right)(0.534\ atm) = 0.370\ atm$$

$$\mathrm{P_{benzene}} = X_{benzene}P°_{benzene} = \left(\frac{0.400}{0.400 + 0.900}\right)(1.34 atm) = 0.412\ atm$$

$$\therefore \mathrm{X_{benzene}} = \frac{0.412}{0.370 + 0.412} = 0.527$$

(b) **2 pts**

$$(0.534\ \mathrm{atm})\mathrm{X_{toluene}} + (1.34\ atm)(1 - X_{toluene}) = 1.00\ atm$$

$$\mathrm{X_{toluene}} = 0.42$$

(c) Benzene will be isolated, since it has higher vapor pressure and lower boiling point. Each time fractional distillation is conducted, benzene will have a higher mole fraction in the vapor phase and will be obtained in a greater amount. **2 pts**

2. (total 8 pts)

Calculate ΔS_{sys}, ΔS_{surr}, and ΔS_{tot} for the irreversible isothermal expansion at 398 K of 1.00 mol of an ideal gas (system) from a pressure of 10.0 atm to constantly held external pressure of 1.00 atm.

(Answer) ΔS_{sys} 3 pts, ΔS_{surr} 4 pts, ΔS_{tot} 1 pt

Since S is a function of state, ΔS_{sys} for the irreversible process is equal to ΔS_{sys} for the reversible process with the same initial and final states.
Thus, $\Delta S_{sys} = q_{rev}/T = -w/T = -[-nRT \ln (V_2/V_1)]/T = -[-nRT \ln (P_1/P_2)]/T = nR \ln (P_1/P_2)$
$= (1.00 \text{ mol})(8.315 \text{ J K}^{-1} \text{ mol}^{-1}) \ln (10.0 \text{ atm}/1.00 \text{ atm})$
$= 19.14 \text{ J K}^{-1}$

ΔS_{surr} = (heat given up by the surrounding)/T = -(heat absorbed by the system)/T
$= -q_{irrev}/T = -(-w_{irrev})/T = (w_{irrev})/T = -P_{ext}\Delta V/T = -(1 \text{ atm})(V_f-V_i)/T$
$V_i = nRT/P_i = (1.00 \text{ mol})(0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1})(398 \text{ K})/10.0 \text{ atm} = 3.24 \text{ L}$
$V_f = nRT/P_f = (1.00 \text{ mol})(0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1})(398 \text{ K})/1.00 \text{ atm} = 32.4 \text{ L}$
Thus,
$\Delta S_{surr} = -(1 \text{ atm})(V_f-V_i)/T = -(1 \text{ atm})(32.4 \text{ L} - 3.24 \text{ L})/398 \text{ K} = -(29.16 \text{ L atm})/398 \text{ K}$
$= -(29.16 \text{ L atm})(101.3 \text{ J}/1 \text{ L atm})/398 \text{ K} = -7.42 \text{ J K}^{-1}$

Hence, $\Delta S_{tot} = \Delta S_{sys} + \Delta S_{surr} = 19.14 \text{ J K}^{-1} + (-7.42 \text{ J K}^{-1}) = 11.72 \text{ J K}^{-1}$

3. (total 10 pts)

Select the alphabet of the correct answer.

a) In a spontaneous process, which of the following always increases?

A) the entropy of the system
B) the entropy of the surroundings
C) the entropy of the universe
D) the entropy of the system and the universe
E) the entropy of the system, surroundings and the universes

b) A process is always spontaneous, regardless of temperature, when ____________ (H and S refer to the system) .

A) $\Delta H > 0$ and $\Delta S < 0$ B) $\Delta H < 0$ and $\Delta S < 0$
C) $\Delta H > 0$ and $\Delta S > 0$ D) $\Delta H < 0$ and $\Delta S > 0$
E) None of these is true, as temperature must always be taken into account.

c) the dissolution of ammonium nitrate in water is a spontaneous endothermic process. It is spontaneous because the system undergoes ____________.

A) a decrease in enthalpy. B) an increase in entropy
C) an increase in enthalpy. D) a decrease in entropy.
E) an increase in free energy.

d) Any reaction will be spontaneous if __________

A) $\Delta G_{sys} > 0$ B) $\Delta G_{sys} < 0$
C) $\Delta H_{sys} > 0$ D) $\Delta S_{sys} < 0$
E) $\Delta H_{sys} < 0$

e) The entropy of vaporization of water is 109.0 J/molK. What is the enthalpy of vaporization of water at its normal boiling point of 100°C?

A) +10.90 kJ/mol
B) -40.66 kJ/mol
C) +3.42 kJ/mol
D) +40.66 kJ/mol
E) -10.90 kJ/mol

Answer
a) C
b) D
c) B
d) B
e) D

4. (total 12 pts)

Substance	△Hf° (KJ/mol)	S° (J/mol·K)
N_2 (g)	0	191.5
H_2 (g)	0	130.6
NH_3 (g)	-46.1	192.6

a) Is the reaction spontaneous in the forward direction at 25℃? Explain it.

$$N_2 (g) + 3 H_2 (g) \rightleftarrows 2 NH_3 (g)$$

b) Estimate the highest temperature at which spontaneity is preserved, assuming that △H° and △S° remain roughly constant throughout.

c) Compute the equilibrium constant at 25℃.

d) Suppose that hydrogen, nitrogen, and ammonia gas are mixed together in a closed vessel, each component having a partial pressure of 4.0 atm. Is the mixture in equilibrium at 25℃? If not, predict in which direction a reaction will proceed.

(Sol)

a) 4 pts (H, S, G, answer each 1 pt)

$$\triangle H^\circ = 2 \triangle H_f{}^\circ[NH_3(g)] - \triangle H_f{}^\circ[N_2(g)] - 3 \triangle H_f{}^\circ[H_2(g)]$$
$$= (2mol)(-46.1\ KJ/K) - 0 - 3 \times (0) = -92.2\ KJ$$
$$\triangle S^\circ = 2\, S^\circ[NH_3(g)] - S^\circ[N_2(g)] - 3\, S^\circ[H_2(g)]$$
$$= 2\ mol\ \times \frac{192.3\ J}{mol \cdot K} - 1\ mol \times \frac{191.5\ J}{mol \cdot K} - 3\ mol \times \frac{130.6\ J}{mol \cdot K}$$
$$= -198.7\ J/K = -0.1987\ KJ/K$$
$$\triangle G^\circ = \triangle H^\circ - T \triangle S^\circ = -92.2\ KJ - (298.15\ K)(-0.1987\ KJ/K)$$
$$= -92.2\ KJ + 59.24\ KJ = -33.0\ KJ$$

The negative sign shows that the reaction is spontaneous.

b) 2 pts

The crossover(△G°=0) is reached when △H°=T△S°.

$$T = \frac{\triangle H^\circ}{\triangle S^\circ} = \frac{-92.2\ KJ}{-0.1987\ KJ/K} = 464\ K$$

The highest possible temperature for a spontaneous reaction.

c) 2 pts

$$K = exp\left(-\frac{\triangle G^\circ}{RT}\right) = exp\left[-\left(\frac{-33.0\ kJ}{(8.3145\ J/K)(298K)}\right) \times \frac{1000\ J}{kJ}\right] = 6.1 \times 10^5$$

d) 4 pts

$$Q = \frac{P_{NH_3}{}^2}{P_{N_2}P_{H_2}{}^3} = \frac{(4.0)^2}{(4.0)(4.0)^3} = 0.062$$

This differs substantially from the equilibrium constant at 25°C (K=6.1x10^5). The mixture is not yet at equilibrium. **2 pts**

There are still too many reactants and too few products (forward). **2 pts**

5. (total 8 pts)

The single step unfolding reaction for many small proteins can be represented by the equilibrium.

$$\text{Folded} \rightleftharpoons \text{Unfolded}$$

The position of this equilibrium changes with temperature; the melting temperature T_m is defined as the temperature at which half of the molecules are unfolded and half are folded. The intensity of the fluorescence signal at a wavelength of 356 nm of a 1.0 µM sample of the protein was measured as a function of temperature over the range 58 to 66 °C:

Temperature (^oC)	58	60	62	64	66
Fluorescence intensity (arbitrary units)	27	30	34	37	40

A 1.0 µM sample in which all of the protein molecules are folded gives a fluorescence signal of 21 units at 356 nm. A 1.0 µM sample in which all of the protein molecules are unfolded gives a fluorescence signal of 43 units. Assuming that the fluorescence intensity from each species is directly proportional to its concentration.

(a) Calculate the fraction, X_{unfold}, of unfolded molecules present at 64 ^oC.

(b) Calculate the equilibrium constant at 64 ^oC.

(c) Estimate the value of T_m for this protein (to the nearest 1 ^oC)

(Answer)

(a)
Because concentration is proportional to the fluorescence intensity (I),

$$I_{tot\ at\ 64\ oC} = 37 = I_{fold} + I_{unfold} = 21X_{fold} + 43\ X_{unfold}$$

$$= 21(1-X_{unfold}) + 43\ X_{unfold}$$

$$X_{unfold} = 0.73 \qquad \textbf{(2 pts)}$$

(b)

$$K = \frac{[\boldsymbol{unfolded}]}{[\boldsymbol{folded}]} = \frac{\boldsymbol{X_{unfolded}}}{\boldsymbol{X_{folded}}} = 0.73/(1\text{-}0.73) = 2.7 \qquad \textbf{(2 pts)}$$

(c)
Calculations of K depending on the given temperatures afford:

Temperature (^oC)	58	60	62	64	66
K	0.38	0.69	1.4	2.7	6.3

At T_m, K =1. Thus, the best estimation of T_m is 61 ^oC. **(4 pts)**

6. (total 7 pts)

Pure water has a pH of 7.00 at 25 °C and 7.27 at 10 °C. Calculate the enthalpy change (ΔH^0) in kJ/mol for the autoionization of water, and predict the pH of pure water at 50 °C.

Answer:

$2H_2O(l) \leftrightarrows H_3O^+(aq) + OH^-(aq)$

$$K_{w,25C} = [H_3O^+][OH^-] = (10^{-pH})^2 = 1.00 \times 10^{-14}$$

$$K_{w,10C} = [H_3O^+][OH^-] = (10^{-pH})^2 = 2.88 \times 10^{-15}$$

$$\ln\left(\frac{K_{w,25C}}{K_{w,10C}}\right) = -\frac{\Delta H^0}{R}\left(\frac{1}{273+25} - \frac{1}{273+10}\right)$$

$$\boldsymbol{\Delta H^0 = 58.2\ kJ/mol}$$

4 pts

$$\ln\left(\frac{K_{w,50C}}{K_{w,25C}}\right) = -\frac{\Delta H^0}{R}\left(\frac{1}{273+50} - \frac{1}{273+25}\right)$$

or

$$\ln\left(\frac{K_{w,50C}}{K_{w,10C}}\right) = -\frac{\Delta H^0}{R}\left(\frac{1}{273+50} - \frac{1}{273+10}\right)$$

$$K_{w,50C} = ([H_3O^+])^2 = 6.16 \times 10^{-14}$$

∴ pH at 50 °C = 6.61

3 pts

7. (total 12 pts)

Calculate pH of given solutions below. (pK_a of HCOOH in water: 3.7, pK_a of HClO in water: 7.5) Both HCOOH and HClO are monoprotic. Assume there is only acid-base reaction and no reaction between two acids.

(a) 0.1 M HCOOH(aq)
(b) 0.1 M HClO(aq)
(c) 0.1 M HCOOH(aq) 100mL + 0.1 M NaOH(aq) 50 mL
(d) 0.1 mM HCOOH(aq) 100mL + 0.1 mM NaOH(aq) 50 mL
(e) 0.3 M HCOOH(aq) 50mL + 0.3 M HClO(aq) 50 mL + 0.3 M NaOH(aq) 50 mL

Answer:

(a) **(2 pts)** For a weak acid, $\mathrm{pH} = -\frac{1}{2}\log(\mathrm{CK_a}) = -\frac{1}{2}\log(0.1) + \frac{3.7}{2} = 2.35$

(b) **(2 pts)** For a weak acid, $\mathrm{pH} = -\frac{1}{2}\log(\mathrm{CK_a}) = -\frac{1}{2}\log(0.1) + \frac{7.5}{2} = 4.25$

(c) **(2 pts)** By NaOH, half of HCOOH became $HCOO^-$. As the amount of HCOOH and its conjugate base are the same, Henderson-Hasselbalch equation gives $\mathrm{pH} = \mathrm{pK_a} + \log\left(\frac{[\mathrm{HCOO^-}]}{[\mathrm{HCOOH}]}\right) = 3.7.$

(d) **(3 pts)** By NaOH, half of HCOOH became $HCOO^-$ and their concentration are 1/30 mM each. After then, HCOOH additionally dissociate to H^+ and $HCOO^-$ to satisfy its K_a. Let $[H^+]$ = x and we obtain the equation,

$$\frac{\left(\frac{1}{30000} + \mathrm{x}\right)\mathrm{x}}{\frac{1}{30000} - \mathrm{x}} = 10^{-3.7}, \mathrm{x} = 2.57 \times 10^{-5}$$

Thus, pH = 4.59.

(e) **(3 pts)** The initial concentration of HCOOH, HClO in a mixed solution is 0.1 M each. Let (final concentration of $HCOO^-$) = x, (that of ClO^-) = y, and (that of H^+) = z. Then, we get a simultaneous equation,

$$\frac{\mathrm{xz}}{\frac{1}{10} - \mathrm{x}} = 10^{-3.7}, \quad \frac{\mathrm{yz}}{\frac{1}{10} - \mathrm{y}} = 10^{-7.5}, \quad \mathrm{x} + \mathrm{y} = \frac{1}{10}$$

$$\text{Since} \quad \frac{1}{10} - x = y \quad and \quad \frac{1}{10} - y = x,$$

$$\frac{\mathrm{xz}}{\mathrm{y}} = 10^{-3.7}, \frac{yz}{x} = 10^{-7.5}$$

$$\therefore \frac{\mathrm{xz}}{\mathrm{y}} \times \frac{yz}{x} = z^2 = 10^{-3.7} \times 10^{-7.5} = 10^{-11.2}$$

By solving this, we can obtain $[H^+] = 2.51 \times 10^{-6}$, thus pH = 5.6.

(Any other solution which yields pH=5.6 will be accepted)

8. (total 6 pts)

Barium sulfate ($BaSO_4$) is used in medical imaging of the gastrointestinal tract. Its solubility product is 1.08×10^{-10} at 25°C, so it is ideally suited for this purpose because of its low solubility when a "barium milkshake" is consumed by a patient. The pathway of the sparingly soluble salt can be easily monitored by x-rays. Will barium sulfate precipitate if 10.0 mL of 0.0020 M Na_2SO_4 is added to 100 mL of 3.2×10^{-4} M $BaCl_2$? Explain why and recall that NaCl is highly soluble in water.

(Answer)

The only slightly soluble salt that can be formed when these two solutions are mixed is $BaSO_4$ because NaCl is highly soluble.

$$BaSO_4(s) \rightleftarrows Ba^{2+}(aq) + SO_4^{2-}(aq)$$

The solubility product expression is as follows:

$K_{sp} = [Ba^{2+}][SO_4^{2-}] = 1.08\times10^{-10}$

The concentrations of Ba^{2+} and SO_4^{2-} are obtained when the number of moles of Ba^{2+} and that of SO_4^{2-} are divided by the final volume (100 mL + 10.0 mL = 110 mL= 0.11 L):

$$[Ba^{2+}] = \frac{(0.100\ L)(3.2 \times 10^{-4}\ mol\ L^{-1})}{0.11\ L} = 2.9 \times 10^{-4}\ M$$

$$[SO_4{}^{2-}] = \frac{(0.010\ L)(2.0 \times 10^{-3}\ mol\ L^{-1})}{0.11\ L} = 1.8 \times 10^{-4}\ M$$

$$Q = [Ba^{2+}][SO_4{}^{2-}] = (2.9 \times 10^{-4})(1.8 \times 10^{-4}) = 5.2 \times 10^{-8}$$

Because $Q > K_{sp}$, we predict that $BaSO_4$ will precipitate when the two solutions are mixed. In fact, $BaSO_4$ will continue to precipitate until the system reaches equilibrium, which occurs when $[Ba^{2+}][SO_4^{2-}] = K_{sp} = 1.08 \times 10^{-10}$.

9. (total 10 pts)

With 100 mL of 1 M HCl and a buffer solution ($1\,\mathrm{M}\ \mathrm{CH_3}COOH\ solution\ 55\ mL$ and $1\ M\ CH_3COONa\ solution\ \ 45\ mL$)

$$\mathrm{Pt}|\mathrm{H_2}(1atm)|H_3O^+(buffer)||H_3O^+(1\ M)|H_2(1atm)|Pt$$

Na^+, CH_3COO^- doesn't participate in cell reactions.
pK_a of $\mathrm{CH_3}COOH$ is 4.74, and molar mass of NaOH is 40 g/mol.

(a) Write anode and cathode half reactions. And calculate the $\mathrm{E_{cell}}$ of the cell.

(b) 0.2 g of NaOH was added to the buffer solution. Calculate the changed $\mathrm{E_{cell}}$.

Solution
(a) **6 pts**
(anode) $\mathrm{H_2}(1atm) + 2H_2O(l) \rightarrow 2H_3O^+(buffer) + 2e^-$
(cathode) $2\mathrm{H_3}O^+(1\ M) + 2e^- \rightarrow H_2(1atm) + 2H_2O(l)$ **(2 pts)**

By using Henderson-Hasselbalch Equation, $\mathrm{pH} = \mathrm{pK_a} - \log_{10}\frac{[CH_3COOH]_0}{[CH_3COO^-]_0}$ =4.65.

$$\mathrm{Q} = \frac{[\mathrm{H_3}O^+(buffer)]^2}{[H_3O^+(HCl)]^2}$$

$$E_{cell} = 0 - \frac{0.0592V}{2}(\log_{10}[\mathrm{H_3}O^+(buffer)]^2 - \log_{10}[H_3O^+(HCl)]^2) = 0.0592\mathrm{V} \times [\mathrm{pH(buffer)}]$$
$$= 0.27528\ V$$
(4 pts)

(b) **4 pts**
First, NaOH 0.2g is 0.005 mol of NaOH.
By reaction $\mathrm{CH_3}COOH(aq) + OH^-(aq) \rightarrow H_2O(l) + CH_3COO^-(\mathrm{aq})$, $moles\ of\ CH_3COOH = 0.055mol - 0.005mol = 0.050mol,$

$moles\ of\ CH_3COO^- = 0.045mol + 0.005mol = 0.050mol$. $\mathrm{pH} = \mathrm{pK_a} - \log\frac{[CH_3COOH]_0}{[CH_3COO^-]_0} = pK_a = 4.74$ **(2 pts)**

So, $\mathrm{E_{cell}} = \frac{0.0592\mathrm{V}}{}\big(pH(buffer)\big) = 0.2806\ \ \mathrm{V}$ **(2 pts)**

10. (total 14 pts)

A student decided to measure the solubility of lead acetate ($Pb(OAc)_2$) in water and sets up the electrochemical cell.

$$Pb|Pb(OAc)_2|OAc^-(aq,\ 0.0500\ M)\ ||\ Cl^-\ (aq,\ 0.500\ M)\ |\ AgCl\ |\ Ag$$

At 25°C, the student finds the cell potential to be 0.546V, and from the textbook he also finds,

$$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq) \qquad E^0 = 0.222\ V$$
$$Pb^{2+}(aq) + 2e^- \rightarrow Pb\ (s) \qquad E^0 = -\ 0.1265\ V$$

(a) What are the electrochemical formula of anode, cathode and net reactions?

4 pts

Anode: $Pb(s) + 2OAc^-\ (aq) \rightarrow Pb(OAc)_2\ (s) + 2\ e^-$ **2 pts**

Cathode: $AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq.)$ **1 pts**

Net: $Pb(s) + 2OAc^-\ (aq) + 2\ AgCl(s) \rightarrow Pb(OAc)_2\ (s) + 2\ Ag(s) + 2\ Cl^-(aq.)$ **1 pts**

(b) Calculate the E^0 of anode, cathode and total cell.

4 pts

Using Nernst equation, $Ecell = E^0cell – 0.0592/n \log Q$

where n=2, and $Q = [Cl-]^2 /[OAc-]^2 = (0.5)^2/(0.05)^2 = 100$

E_{cell} measured as 0.546V, $E_{cell}{}^0 = E_{cell} + 0.0592/n \log Q = 0.546 + 0.0592 = 0.6052V$

Since, $E_{cell}{}^0 \ = E^0{}_{cathode} - E^0{}_{anode}$

$E^0{}_{cathode} = 0.222V$, $E^0{}_{anode}$ becomes -0.3832V

(c) What does the student find for the K_{sp} of $Pb(OAc)_2$? (Write the net reaction)

6 pts

Anode $Pb(s) + 2OAc^-\ (aq) \rightarrow Pb(OAc)_2\ (s) + 2\ e^-$

Cathode $Pb^{2+}(aq.) + 2e^- \rightarrow Pb\ (s)$

Net $Pb^{2+}(aq.) + 2OAc^-\ (aq) \rightarrow Pb(OAc)_2\ (s)$ ---- **2 pts**

$E^0{}_{cell} = -0.1265 – (-0.3832)$

= 0.2567V ------**1 pt**

$\Delta G^0{}_{cell} = -nFE^0cell = -(2mol)(96485\ C\ mol^{-1--})(0.2567) = -49.535\ kJ$ ---------**1 pt**

ΔG^0 of the dissolution reaction of $Pb(OAc)_2(s)$ is 49.535 kJ, $K_{sp} = \exp(-\Delta G^0/RT) = \exp(-49535J / (8.314 * 298.15) = 2.10x\ 10^{-9}$ ----------------------**2 pts**

11. (total 6 pts)

Lithium cobalt oxide and specialty carbon are active ingredients for the positive and negative electrodes, respectively, of a rechargeable lithium battery. During the charge recharge cycles, the following reversible half-reactions occur.

$LiCoO_2 \rightleftharpoons Li_{1-x}CoO_2 + x\ Li^+ + x\ e^-$

$C + x\ Li^+ + x\ e- \rightleftharpoons CLi_x$

Graphite has lithium intercalation sites between its layers. Assuming a maximum 6:1 carbon-to-lithium intercalation stoichiometry, calculate the theoretical charge capacity of 1.00 gram of graphite to intercalate lithium. Answer in mAh/g. The total amount of energy a battery can store (charge capacity) is rated in mAh. For example, a battery rated at 1500 mAh can power a device drawing 100 milliamps for 15 hours.

(Answer)
1.00 g graphite (C) = 0.0833 mol carbon
6 mol carbon to 1 mol lithium; 1 g graphite can hold 0.0139 mol lithium

To insert 1 mol lithium, 96487 coulombs are needed.
Therefore, 1 g graphite can charge 96487 × 0.0139 = 1340 coulombs.
1340 coulombs / g = 1340 A sec / g
= 1340 × 1000 mA × (1 / 3600) h = 372 mAh / g (6 pts)

Physical Constants

Avogadro's number	N_A = 6.02214179 x 10^{23} mol^{-1}
Bohr radius	a_0 = 0.52917720859 Å = 5.2917720859 x 10^{-11} m
Boltzmann's constant	K_B = 1.3806504 x 10^{-23} J K^{-1}
Electronic charge	e = 1.602176487 x 10^{-19} C
Faraday constant	F = 96485.3399 C mol^{-1}
Masses of fundamental particles:	
Electron	m_e = 9.10938215 x 10^{-31} kg
Proton	m_P = 1.672621637 x 10^{-27} kg
Neutron	m_n= 1.674927211 x 10^{-27} kg
Permittivity of vacuum	ε_o = 8.854187817 x 10^{-12} C^{-2} J^{-1} m^{-1}
Planck's constant	h = 6.62606896 x 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 x 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 x 10^{-27} kg
	1 u = 1.492417830 x 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 x 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 x 10^{-18}J = 1312.7136 kJ mol^{-1} = 13.60569193 eV
Standard atmosphere	1 atm = 1.01325 x 10^{5} Pa = 1.01325 x 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)

Claim Form for General Chemistry Examination

Page (/)

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