2015 Fall Semester Midterm
For General Chemistry I (CH101)

Date: October 21 (Wed), Time Limit: 19:00 ~ 21:45

Student I.D. Number	Name

75 Normal Points + 8 Bonus Points

If you get 75 points out of 83 points, you will get the full 40% assigned to the mid-term exam. We suggest that you skim through all the problems quickly. There are some straightforward problems whose solution you can easily write down without much calculation.

Your scores

1)	out of 7
2)	out of 8
3)	out of 7
4)	out of 11
5)	out of 6
6)	out of 11
7)	outof 8
8)	out of 4
9)	out of 4
10)	out of 17

Total:	out of **83**

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

1. Period, Location, and Procedure

1) Return and Claim Period: ***October 26 (Mon, 19: 00 ~ 20:00 p.m.)***
2) ***Location: Room for quiz session***
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 paperback 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 10/26 on the web.)

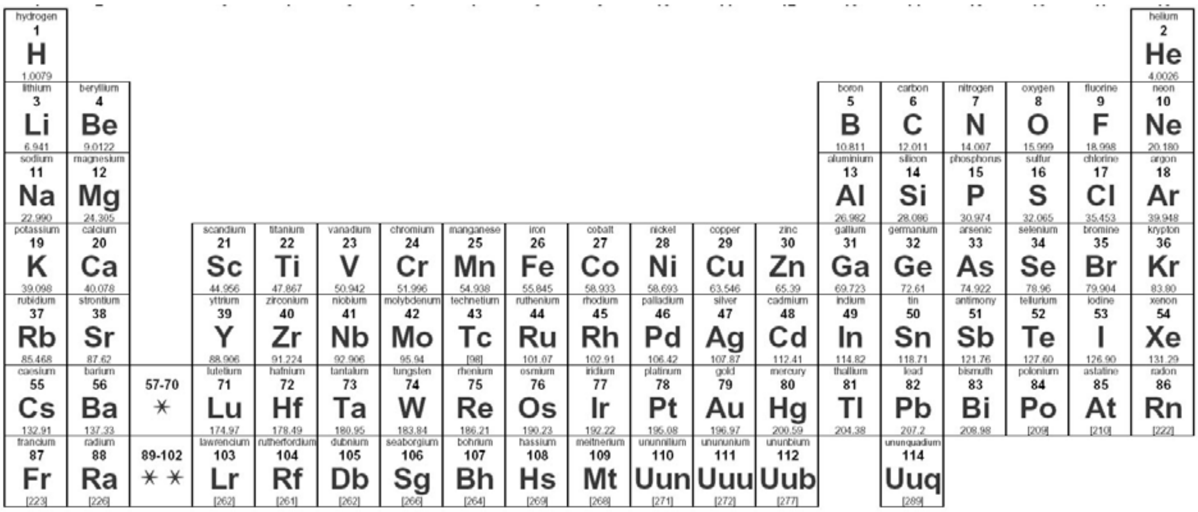
2. Final Confirmation

1) Period: ***October*** 29 (Thu) –***October***30 (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.***

You may refer to the following information.



hydrogen 1 H 1.0079																		helium 2 He 4.0026
lithium 3 Li 6.941	beryllium 4 Be 9.0122												boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180
sodium 11 Na 22.990	magnesium 12 Mg 24.305												aluminium 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948
potassium 19 K 39.098	calcium 20 Ca 40.078		scandium 21 Sc 44.956	titanium 22 Ti 47.867	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.39	gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80
rubidium 37 Rb 85.468	strontium 38 Sr 87.62		yttrium 39 Y 88.906	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	molybdenum 42 Mo 95.94	technetium 43 Tc [98]	ruthenium 44 Ru 101.07	rhodium 45 Rh 102.91	palladium 46 Pd 106.42	silver 47 Ag 107.87	cadmium 48 Cd 112.41	indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29
caesium 55 Cs 132.91	barium 56 Ba 137.33	57-70 *	lutetium 71 Lu 174.97	hafnium 72 Hf 178.49	tantalum 73 Ta 180.95	tungsten 74 W 183.84	rhenium 75 Re 186.21	osmium 76 Os 190.23	iridium 77 Ir 192.22	platinum 78 Pt 195.08	gold 79 Au 196.97	mercury 80 Hg 200.59	thallium 81 Tl 204.38	lead 82 Pb 207.2	bismuth 83 Bi 208.98	polonium 84 Po [209]	astatine 85 At [210]	radon 86 Rn [222]
francium 87 Fr [223]	radium 88 Ra [226]	89-102 * *	lawrencium 103 Lr [262]	rutherfordium 104 Rf [261]	dubnium 105 Db [262]	seaborgium 106 Sg [266]	bohrium 107 Bh [264]	hassium 108 Hs [269]	meitnerium 109 Mt [268]	ununnilium 110 Uun [271]	unununium 111 Uuu [272]	ununbium 112 Uub [277]		ununquadium 114 Uuq [289]				

Planck constant(h) = 6.626×10^{-34} J·s

Elementary charge(e) = 1.602×10^{-19}C

Vacuum permittivity (ε_0)= $8.854\times10^{-12}\mathrm{J}^{-1}\cdot\mathrm{C}^{2}\mathrm{m}^{-1}$

Electron mass(m_e) = 9.109×10^{-31}kg

Speed of light in vacuum(c) = 2.998×10^{8}m/s

Rydberg constant = 3.29 x 10^{15} /s^{1}

$$\int d\tau = \int_0^\infty \int_0^\pi \int_0^{2\pi} r^2 dr \sin\theta d\theta d\phi$$

$$\int \sin^2 ax \, dx = \frac{x}{2} - \frac{1}{4a}\sin 2ax + C = \frac{x}{2} - \frac{1}{2a}\sin ax \cos ax + C$$

$$\int \sin^3 ax \, dx = \frac{\cos 3ax}{12a} - \frac{3\cos ax}{4a} + C$$

$$\int x \sin^2 ax \, dx = \frac{x^2}{4} - \frac{x}{4a}\sin 2ax - \frac{1}{8a^2}\cos 2ax + C$$

$$\int x^2 \sin^2 ax \, dx = \frac{x^3}{6} - \left(\frac{x^2}{4a} - \frac{1}{8a^3}\right)\sin 2ax - \frac{x}{4a^2}\cos 2ax + C$$

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

$$E_n = \frac{h^2 n^2}{8ma^2} \text{ , } n = 1, 2, \ldots,$$

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

$$\sin 2x = 2\sin x \cos x$$

$$\cos 2x = \cos^2 x - \sin^2 x = 2\cos^2 x - 1 = 1 - 2\sin^2 x$$

$$\tan 2x = \frac{2\tan x}{1 - \tan^2 x}$$

$$\frac{\tan^2 x - 1}{\tan x} = \frac{-2}{\tan 2x}$$

$$\cot 2x = \frac{\cot^2 x - 1}{2\cot x}$$

$$\cos^2 x = \frac{1 + \cos 2x}{2}$$

$$\sin^2 x = \frac{1 - \cos 2x}{2}$$

$$\sin^3 x = \frac{3\sin x - \sin 3x}{4}$$

$$\cos^3 x = \frac{3\cos x + \cos 3x}{4}$$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi = E\psi$$

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

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

$$\Delta x \Delta p > \frac{h}{2\pi}$$

$$E(\lambda, T) = \frac{2hc^2}{\lambda^5} * \frac{1}{e^{\left(\frac{hc}{\lambda kT}\right)} - 1}$$

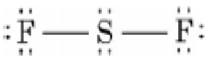
1. Answer the following questions. (Total 7 pts)

(a) Draw the Lewis diagram of SF_2 and write the formal charges on all atoms. (2 pts)

*1 pt for correct Lewis diagram, and 1 pt for correct formal charges. Otherwise no partial points.

Answer)

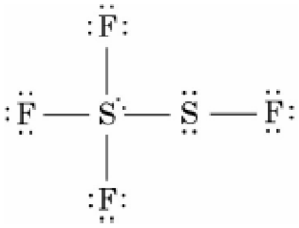
0 0 0



(b) Draw the Lewis diagram of F_3S-SF and write formal charges on all atoms. (3 pts)

*2 pts for correct Lewis diagram, 1 pt for correct formal charges. Otherwise no partial points.

Answer)

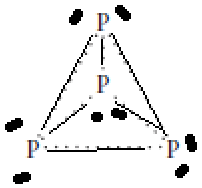


, All formal charges= 0

(c) Draw the 3D Lewis structure of white phosphorus P_4. The lone pairs must be shown. (2 pts)

*No partial points.

Answer)

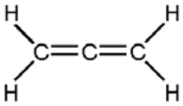


2. Answer the following questions. (Total 8 pts)

(a) Draw the Lewis diagram of allene, H_2CCCH_2. (2 pts)

*No partial points.

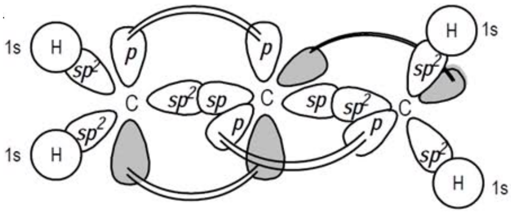
Answer)



(b) Draw the 3D structure of allene. Indicate whether the four H atoms are in the same plane or not. Explain your answerusing hybrid orbitals. (4 pts)

*1pt for the correct 3D structure, 3pts for correct explanation using hybrid orbitals.

Answer)



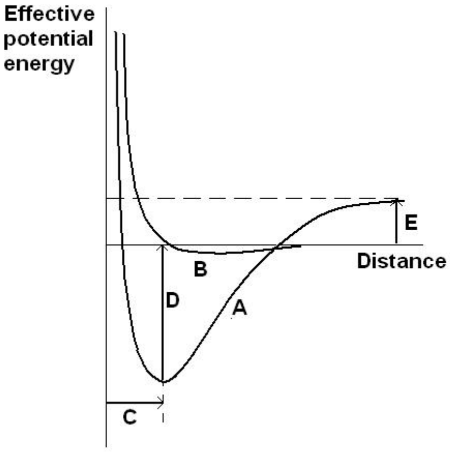
(c) Write down two conditions for significant orbital mixing in MO construction. (2 pts)

*1 pt for each.

Answer)

(1) two atomic orbitals contribute significantly to bond formation only if their atomic energy levels are very close to each other. (2) Two atomic orbitals on different atoms contribute significantly to bond formation only if they overlap significantly.

3. The following diagram illustrates the potential energy of the ions K^+ and F^-, and the atoms K and F, as a function of their inter-nuclear separation (all in the gas phase). (Total 7 pts)



(a) What does the curve A represent? (1 pt) *No partial points.

Answer)

A: K^+ + F^- Curve

(b) What does the curve B represent? (1 pt) *No partial points.

Answer)

B: K + F Curve

(c) What does the Energy D represent? (1 pt) *No partial points.

Answer)

D: Bond dissociation energy of KF

(d)What does the Energy E represent? (1 pt) *No partial points.

Answer)

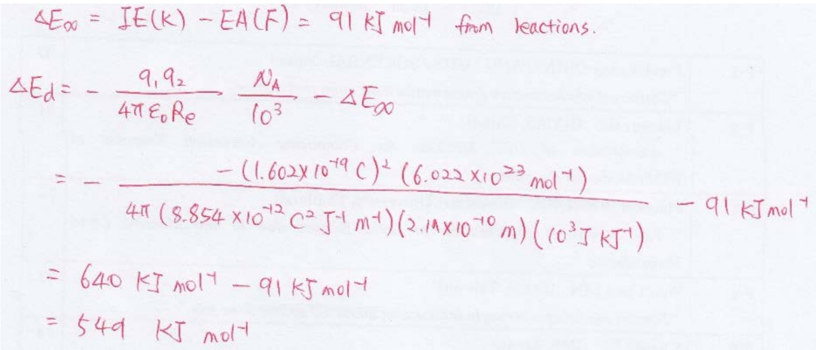
E:IE of K – EA of F

(e) Calculate the energy of dissociation to neutral atoms for KF, which has a bond length of 2.17 ×10^{-10} m. Consider the following reactions. Express you answer in kJ/mol. (q = 1.602 x 10^{-19} C, N_A = 6.022 x 10^{23} mol^{-1}, $\in_0$ = 8.854 x 10^{-12} C^2 J^{-1} m^{-1}) (3 pts)

$K \rightarrow K^+ + e^-$ ΔE = 419 kJ mol^{-1}
$F + e^- \rightarrow F^-$ ΔE = -328 kJ mol^{-1}

*2 pt for correct equations and 1 pt for correct final answer.

Answer)



$\Delta E_\infty = IE(K) - EA(F) = 91\ \text{KJ mol}^{-1}$ from reactions.

$$\Delta E_d = -\frac{q_1 q_2}{4\pi \varepsilon_0 R_e}\frac{N_A}{10^3} - \Delta E_\infty$$

$$= -\frac{-(1.602\times10^{-19}\ C)^2 (6.022\times10^{23}\ \text{mol}^{-1})}{4\pi(8.854\times10^{-12}\ C^2 J^{-1} m^{-1})(2.17\times10^{-10}\ m)(10^3 J\ KJ^{-1})} - 91\ \text{KJ mol}^{-1}$$

$= 640\ \text{KJ mol}^{-1} - 91\ \text{KJ mol}^{-1}$

$= 549\ \text{KJ mol}^{-1}$

4. Answer the following questions about a particle-in-a-box. (Total 11 pts)

(a) We get $\psi(x) = \mathrm{A}\sin\left(\frac{n\pi x}{L}\right)$ solving the differential equation. Normalize $\psi(x)$ and show how we can derive $E_n = \frac{h^2 n^2}{8ma^2}$. (2 pts)

*No partial points.

Answer)

$$\mathrm{A}^2\int_0^L \sin 2\left(\frac{n\pi x}{L}\right)dx = \mathrm{A}^2\left(\frac{L}{2}\right) = 1,\ \mathrm{A} = \sqrt{\frac{2}{L}}\psi n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)n = 1, 2, 3, \dots$$

$$\frac{d2\psi n(x)}{dx2} = -\left(\frac{n\pi}{L}\right)^2\psi n(x) = -\frac{8\pi 2mE}{h2}\psi(x)En = \frac{n2h2}{8mL2}n = 1, 2, 3, \dots$$

(b) What is the probability that the particle will lie between x=0 and x=L/4 if the particle is in its n=2 state? (3 pts)

*1 pt for the correct equation and 2 pts for the correct final answer.

Answer)

Copy the wave-function for a particle in a one-dimensional box (given in the problem) letting $n = 2$, and letting the length of the box equal 1 unit $(L = 1)$

$$\psi_2 = \sqrt{\frac{2}{L}} \sin 2\pi x = \sqrt{2} \sin 2\pi x$$

Letting $L = 1$ de-clutters the mathematics but does not affect the shapes of the functions, which are the subject of the problem. The shape of ψ_2 appears in text Figure 4.26 (b) on text page 172. As the figure shows, ψ_2 has a node at $x = \frac{1}{2}$. The node appears because $\sqrt{2}\sin 2\pi x$ equals zero if $x = \frac{1}{2}$ (recall that $\sin\pi = \sin 180° = 0$). The wave-function ψ_2 has a maximum at $x = \frac{1}{4}$ and a minimum at $x = \frac{3}{4}$ because the sine function has a maximum at $\pi/2 = 90°$ and a minimum at $3\pi/2 = 270°$. The square of the wave-function is proportional to the probability of finding the particle at different values of x. As text Figure 4.26 (c) shows, the function $(\psi_2)^2$ equals zero at $x = \frac{1}{2}$ and has symmetrical maxima at $x = \frac{1}{4}$ and $\frac{3}{4}$. Inspection of the figure (or consideration of the symmetry of the sine-squared function) shows that the region between $x = 0$ and $x = \frac{1}{4}$ accounts for one-fourth of the area under the curve. Since the probability is 1 that the particle is in the box somewhere, the answer is $\frac{1}{4} \times 1 = \boxed{\frac{1}{4}}$.

Tip. The same answer is obtained by integrating $(\psi_2)^2$ and evaluating the integral over the interval $x = 0$ to $x = 1/4$

$$\text{probability} = \int_0^{1/4} (\psi_2)^2\, dx = \int_0^{1/4} \left(\sqrt{2}\sin 2\pi x\right)^2 dx = 2\int_0^{1/4} \sin^2 2\pi x\, dx$$

From a table of integrals

$$\int \sin^2 ax\, dx = \frac{x}{2} - \frac{\sin 2ax}{4a}$$

After substituting $a = 2\pi$, evaluation of the integral follows the procedure explained in calculus books

$$\text{probability} = 2\left|\frac{x}{2} - \frac{\sin(4\pi x)}{8\pi}\right|_{x=0}^{x=1/4}$$

$$= 2\left[\left(\frac{1/4}{2} - \frac{0}{2}\right) - \left(\frac{-\sin\pi}{8\pi} - \frac{-\sin 0}{8\pi}\right)\right] = 2\left[\frac{1}{8} - 0 + 0 - 0\right] = \frac{1}{4}$$

(c) Write the wave function for a particle in a rectangular box of length L on x axis, 2L on y-axis, and 3L on z-axis direction, with one corner located at the origin of coordinates. (2 pts)

*No partial points.

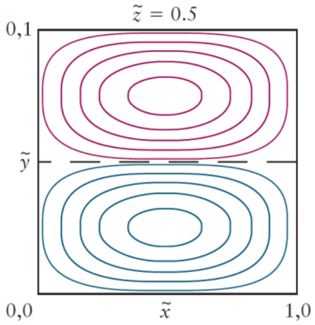
Answer)

$$\Psi_{n_x n_y n_z}(x, y, z) = \left(\frac{4}{3L^2}\right)^{\frac{1}{2}} \sin\left(\frac{n_x \pi x}{L}\right) \sin\left(\frac{n_y \pi y}{2L}\right) \sin\left(\frac{n_z \pi z}{3L}\right)$$

(d) Continuing from (c), $\tilde{x}, \tilde{y}, \tilde{z}$ are dimensionless variables which range from 0 to 1.

$$\widetilde{\Psi} = \frac{(value\ of\ \Psi)}{(maxium\ value\ of\ \ \Psi)}, \tilde{x} = \frac{x}{L}$$

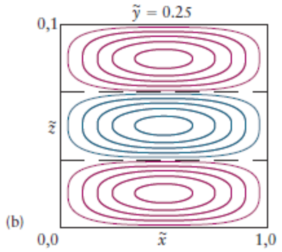
The following graph shows a contour plot of $\widetilde{\Psi}_{123}(\tilde{x}, \tilde{y}, \tilde{z})$ at a cut plane of $\tilde{z} = 0.5$.



Draw the contour plot at a cut plane of $\tilde{y} = 0.25$. Specify the axis and nodal planes as in the above example. (2 pts)

*No partial points. If you do not indicate the axis, no points.

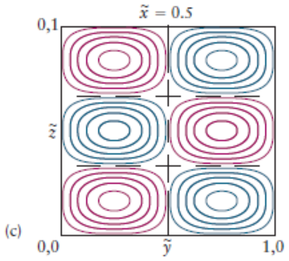
Answer)



(e) Continuing from (d), draw the contour plots at a cut plane of $\tilde{x} = 0.5$. Specify the axis and nodal planes like the example above. (2 pts)

*No partial points. If you do not indicate the axis, no points.

Answer)

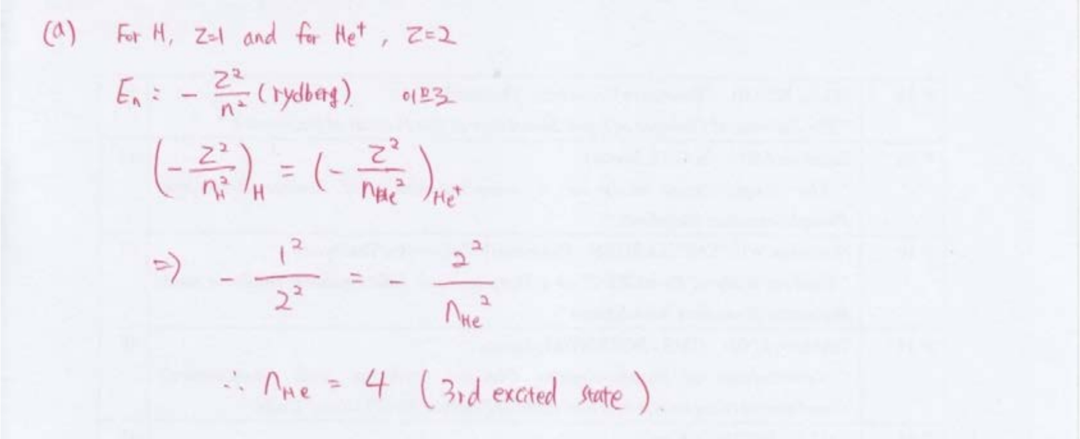


5. Answer the following questions. (Total 6 pts)

(a) Use the Bohr model to determine the excited electronic state of He^+ that has the same energy as the first excited state of hydrogen. (2 pts)

*No partial points.

Answer)



(a) For H, $Z=1$ and for He^+, $Z=2$

$E_n = -\frac{Z^2}{n^2}(\text{rydberg})$ 이므로

$$\left(-\frac{Z^2}{n_H^2}\right)_H = \left(-\frac{Z^2}{n_{He}^2}\right)_{He^+}$$

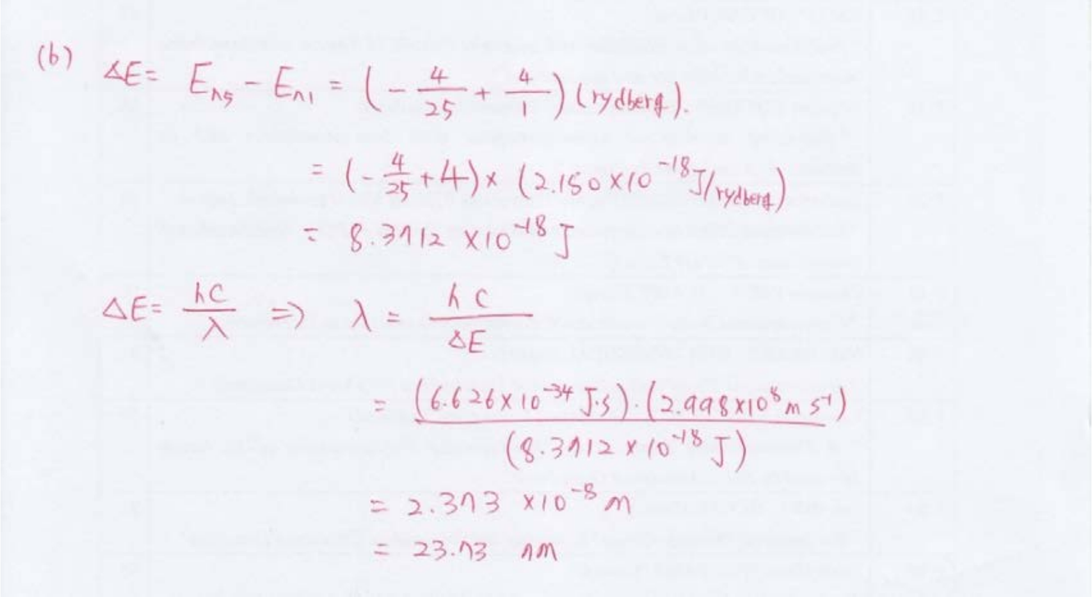
$$\Rightarrow \quad -\frac{1^2}{2^2} = -\frac{2^2}{n_{He}^2}$$

$$\therefore n_{He} = 4 \quad (\text{3rd excited state})$$

(b) Use the Bohr model to calculate the wavelength (in nm) of the light emitted in a transition from the n=5 state to the ground state of this ion. (2 pts)

*No partial points.

Answer)



(b) $$\Delta E = E_{n_5} - E_{n_1} = \left(-\frac{4}{25} + \frac{4}{1}\right)(\text{rydberg}).$$

$$= \left(-\frac{4}{25} + 4\right) \times (2.150 \times 10^{-18}\ \text{J/rydberg})$$

$$= 8.3912 \times 10^{-18}\ \text{J}$$

$$\Delta E = \frac{hc}{\lambda} \Rightarrow \lambda = \frac{hc}{\Delta E}$$

$$= \frac{(6.626 \times 10^{-34}\ \text{J}\cdot\text{s})\cdot(2.998 \times 10^{8}\ \text{m s}^{-1})}{(8.3912 \times 10^{-18}\ \text{J})}$$

$$= 2.393 \times 10^{-8}\ \text{m}$$

$$= 23.93\ \text{nm}$$

(c) What is the limitation of the Bohr model? (2 pts)

*Partial points may be given depending on your answer.

Answer)

Limitation: Bohr’s model cannot account for the spectra of many-electron atoms.

6.Answer the following questions. (Total 11 pts)

(a) Predict the atomic number of the 9th period-element of group 1 (Group 1 includes H, Li, Na and so on). (3 pts)

*No credit for incorrect explanation, 1ptfor wrong answer but correct explanation.

Answer)

7thperiod element: ^{87}Fr

8thperiod element: 86+2(7s)+14(5f)+10(6d)+6(7p)+1=119

9thperiod element: 118+2(8s)+18(5g)+14(6f)+10(7d)+6(8p)+1=169 => answer is 169

(b) Which has the larger third ionization energy, C or N, and why? (2 pts)

*Partial points may be given depending on your answer.

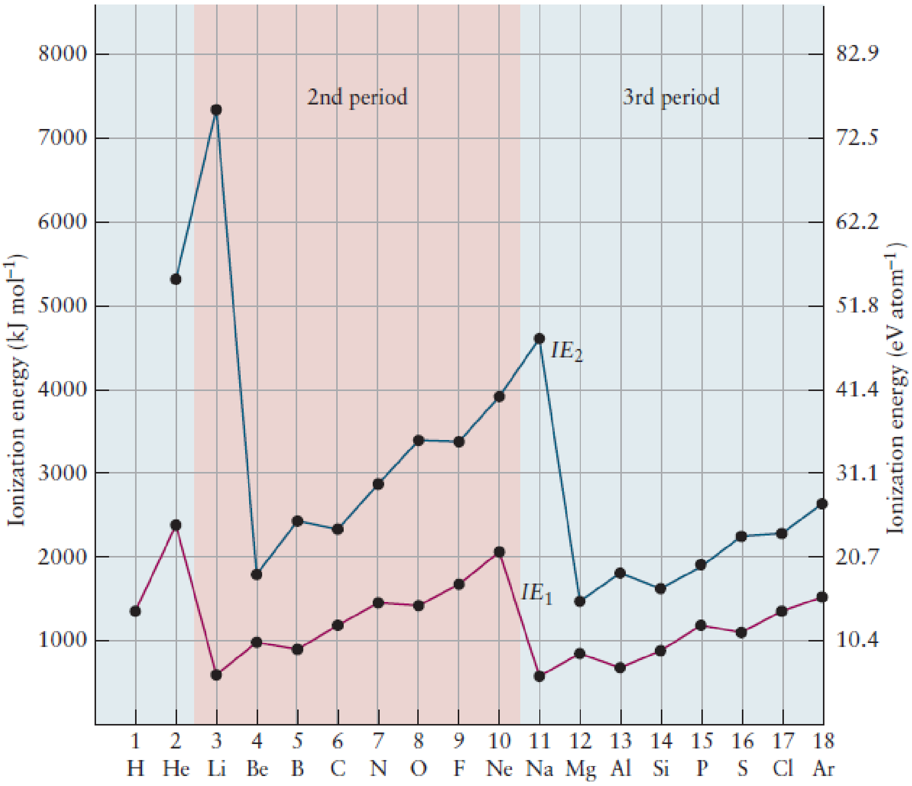
Answer)

The first and second ionization of each removes a 2p electron, but the third removes a 2s electron from C, but only another 2p electron from N. The change in subshell with C means it has the higher second ionization energy.

C has the larger third EA: 1pt

Difference between 2s and 2p orbitals: 1pt

(c) The following graph illustrates the first and second ionization energies of atoms of the first three periods.



The first ionization energy of Li is smallest in the 2nd period atoms, but the second ionization energy of Li is biggest in 2nd period atoms. Explain the reason. (2 pts)

*Partial points may be given depending on your answer.

Answer)

The 2nd ionization energy of Li is the energy required to remove an electron from an inner shell (change of shell), so it is drastically increased.

The decrease of n from 2 to 1: 2pt,

Without the mention about n, just general trend of IE_1 of 2nd period atoms: 1pt

(d) The second ionization energy of O is bigger than that of N, but the first ionization energy of O is smaller than N. Explain the reason. (2 pts)

*Partial points may be given depending on your answer.

Answer)

N has 1 electrons in each 2p orbitals, but O has 1 more electron, so one of the electrons in 2p orbitals is paired, and due to the repulsion, it is more easy to get rid an electron from O than N. **Repulsion between paired electrons on 2p orbital: 2pt**

Without the mention about repulsion, just stability between orbitals: 1pt

(e) Consider the elements aluminum (Al) and silicon (Si). Choose which has the higher electron affinity and explain the reason. (2 pts)

*Partial points may be given depending on your answer.

Answer)

Silicon has higher affinity. Al and Si have neither paired electrons nor half-filled orbitals, so electron affinity of them depend on effective nuclear charge. Z_{eff} of Si is greater than Al.

Si has the higher EA: 1pt

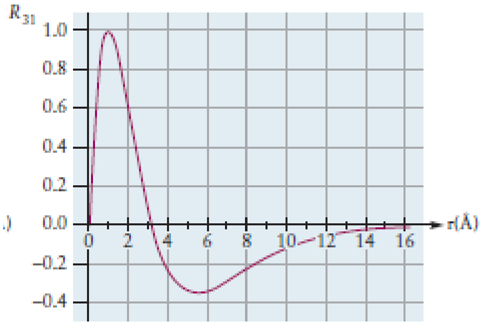
Z_{eff} or stability of orbitals: 1pt

7. Answer the following questions. (Total 8 pts)

(a) Draw the radial wave function of a 3p orbital against the distance from the nucleus. (2 pts)

*No partial points.

Answer)



(b) How many angular nodes does the 3p orbital have? (2 pts)

*No partial points.

Answer)

One.

(c) What is the total number of nodes of the 3p orbital? (2 pts)

*No partial points.

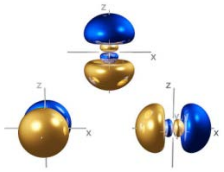
Answer)

Two.

(d) Draw the 3p orbital. Nodes have to be clearly shown and the sign of amplitudes need to be clearly specified. (2 pts)

*No partial points.

Answer)



(Nodes have to be clearly shown)

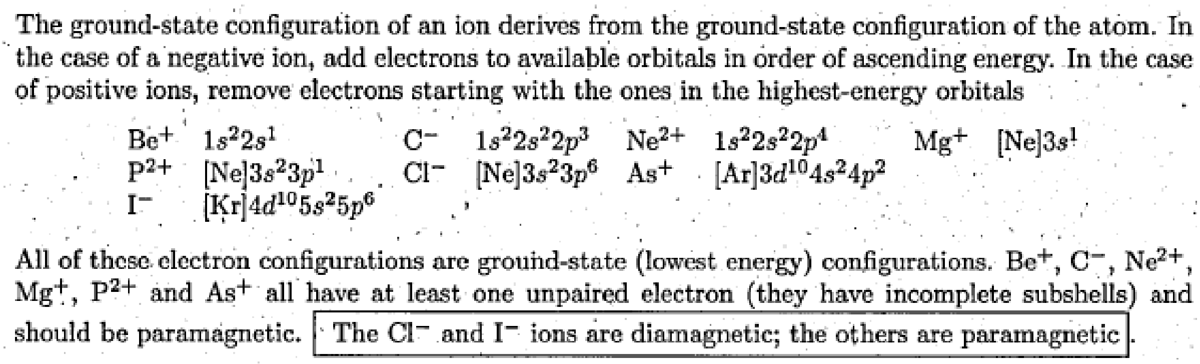
Only one of these is enough.

8. Write ground-state electron configurations for the ions Be^+,C^-, Ne^{2+}, Mg^+, P^{2+}, Cl^-, As^+, and I^-. Which do you expectwill be paramagnetic due to the presence of unpaired electrons? (4 pts)

*0.25 pts for electron configurations, 2 pts for finding out the diamagnetic atoms.

*0 pt if the electron configuration is wrong even if the answer for diamagnetic atoms is right.

Answer)

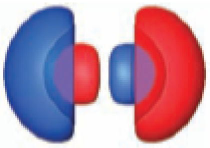
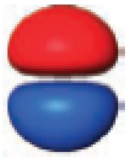
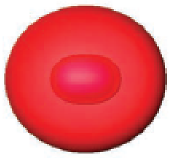
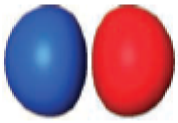
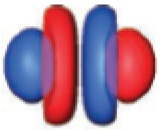
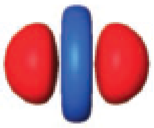
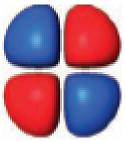


The ground-state configuration of an ion derives from the ground-state configuration of the atom. In the case of a negative ion, add electrons to available orbitals in order of ascending energy. In the case of positive ions, remove electrons starting with the ones in the highest-energy orbitals

Be^+	$1s^22s^1$	C^-	$1s^22s^22p^3$	Ne^{2+}	$1s^22s^22p^4$	Mg^+	$[Ne]3s^1$
P^{2+}	$[Ne]3s^23p^1$	Cl^-	$[Ne]3s^23p^6$	As^+	$[Ar]3d^{10}4s^24p^2$		
I^-	$[Kr]4d^{10}5s^25p^6$						

All of these electron configurations are ground-state (lowest energy) configurations. Be^+, C^-, Ne^{2+}, Mg^+, P^{2+} and As^+ all have at least one unpaired electron (they have incomplete subshells) and should be paramagnetic. The Cl^- and I^- ions are diamagnetic; the others are paramagnetic.

9. This picture is the eight lowest energy molecular orbitals of H_2^+. Write the number written next to each orbitals in the order of increasing energy, starting from the lowest energy orbital. (4 pts)

 1	 2	 3	 4
 5	 6	 7	 8

Answer) 1 5 4 2 3 7 8 6

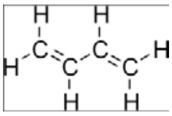
***2pts if they get ranking 1~4 right.**

10. Answer the following questions. (Total 17 pts)

(a) Draw the Lewis structure of $CH_2CHCHCH_2$. (1 pt)

*No partial points.

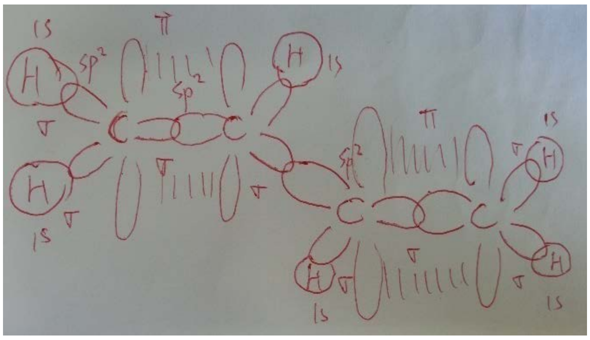
Answer)



(b) Draw the 3Dstructure of butadiene and explain it by using hybrid orbitals. Mark every bonding whether it isσ or π, and write the names of hybrid orbitals. (2 pts)

*1 pt for correct hybridization, 1 pt for correct naming of bonds.

Answer)



(c) Write down the wavefunction for the sigma bond between the first two C atoms using Valence Bond Theory. (2 pts)

*No partial points.

Answer)

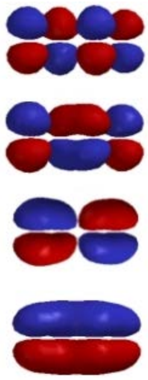
When sp^2 orbital of C^A is $\chi_1^A r, \chi_2^A r, \chi_3^A(r)$,

$$\Psi_\sigma^{bond}(1,2) = C[\chi_1^A(1)\chi_1^B(2) + \chi_1^A(2)\chi_1^B(1)]$$

(d) There are four p orbitals that can interact with each other in butadiene. Draw the four MOs that you can obtain using these four AOs and label them in the order of increasing energy. (3 pts)

*2 pts for correct MO, 1 pt for correct ordering.

Answer)



(d) How many electrons occupy these MOs? (2 pts)

*No partial points.

Answer)

4 electrons

(e) Butadiene molecule can be simplified asa problem of a particle-in-a-box. Rationalize this simplification. (3 pts)

*Partial points may be given depending on your answer.

Answer)

4 electrons are delocalized onto the whole butadiene molecule by the four pi-interacting p orbitals, so it can be considered as a box, containing 4 electrons as its particles.

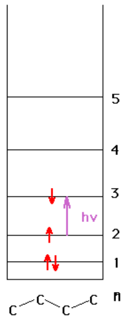
***Key word: delocalization, electron=particle**

(f) Predict the wavelength of the lowest-energy light that ground state butadiene can absorb by simplifying butadiene asa particle-in-a-box model. Consider butadiene as a linear molcule (not bent) for simple calculations.Use the following table if necessary. (4 pts)

*1 pt for the correct box length, 1 pt for the correct equation. 2 pts for the correct final answer.

C–C	Length (pm)
sp^3–sp^3	154
sp^3–sp^2	150
sp^2–sp^2	147
sp^3–sp	146
sp^2–sp	143
sp–sp	137

Answer)



$$\Delta E = (n_2^2 - n_1^2)\frac{h^2}{8mL^2} = (9-4)\frac{(6.626\times10^{-34})^2}{8\times(9.109\times10^{-31})\times(147\times3\times10^{-12})^2} = 1.549\times10^{-18}\ \mathrm{J}$$

$$\lambda = \mathrm{h}\frac{c}{E} = 6.626\times10^{-34}\times\frac{3\times10^{8}}{1.637\times10^{-18}} = 128.3\ nm$$

Claim Form for General Chemistry Examination

Page (/)

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

2015 Fall Semester Final Exam
For General Chemistry I (CH101)

Date: December 16 (Wed),   Time Limit: 19:00 ~ 21:45

Student I.D. Number	Name

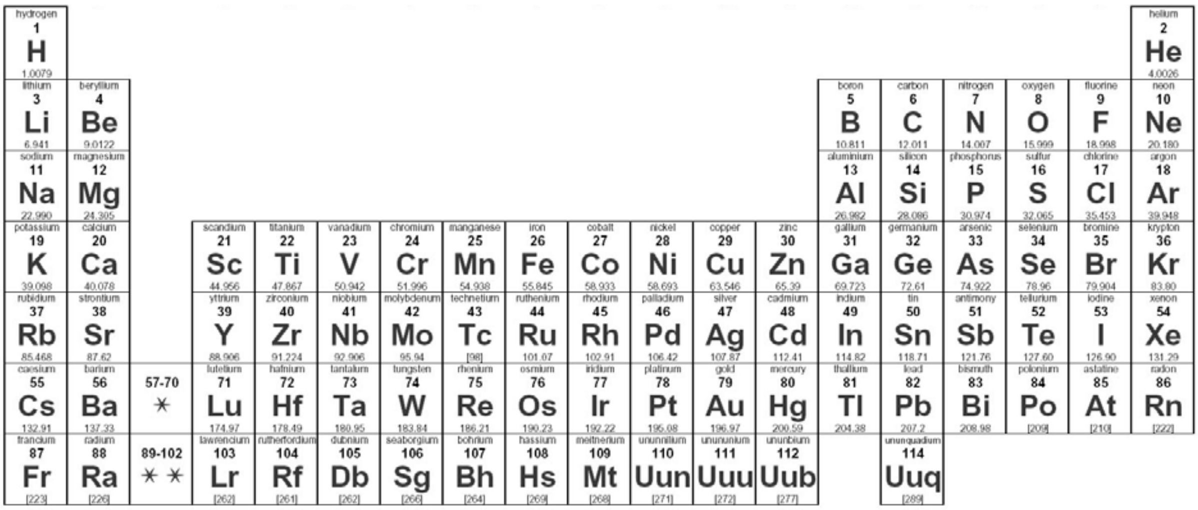
125 Normal Points + 31 Bonus Points

If you get 120 points out of 156 points, you will get the full 60% (or your requested percentage choice) assigned to the mid-term exam. We suggest that you skim through all the problems quickly. There are some straightforward problems whose solution you can easily write down without much calculation.

Your scores

Problem #	Your Score	Full Score
1		9
2		10
3		15
4		15
5		14
6		15
7		13
8		12
9		17
10		12
11		24
Total		156

You may refer to the following information.



hydrogen 1 H 1.0079																		helium 2 He 4.0026
lithium 3 Li 6.941	beryllium 4 Be 9.0122												boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180
sodium 11 Na 22.990	magnesium 12 Mg 24.305												aluminium 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948
potassium 19 K 39.098	calcium 20 Ca 40.078		scandium 21 Sc 44.956	titanium 22 Ti 47.867	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.39	gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80
rubidium 37 Rb 85.468	strontium 38 Sr 87.62		yttrium 39 Y 88.906	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	molybdenum 42 Mo 95.94	technetium 43 Tc [98]	ruthenium 44 Ru 101.07	rhodium 45 Rh 102.91	palladium 46 Pd 106.42	silver 47 Ag 107.87	cadmium 48 Cd 112.41	indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29
caesium 55 Cs 132.91	barium 56 Ba 137.33	57-70 *	lutetium 71 Lu 174.97	hafnium 72 Hf 178.49	tantalum 73 Ta 180.95	tungsten 74 W 183.84	rhenium 75 Re 186.21	osmium 76 Os 190.23	iridium 77 Ir 192.22	platinum 78 Pt 195.08	gold 79 Au 196.97	mercury 80 Hg 200.59	thallium 81 Tl 204.38	lead 82 Pb 207.2	bismuth 83 Bi 208.98	polonium 84 Po [209]	astatine 85 At [210]	radon 86 Rn [222]
francium 87 Fr [223]	radium 88 Ra [226]	89-102 * *	lawrencium 103 Lr [262]	rutherfordium 104 Rf [261]	dubnium 105 Db [262]	seaborgium 106 Sg [266]	bohrium 107 Bh [264]	hassium 108 Hs [269]	meitnerium 109 Mt [268]	ununnilium 110 Uun [271]	unununium 111 Uuu [272]	ununbium 112 Uub [277]		ununquadium 114 Uuq [289]				

Planck constant(h) = 6.626×10^{-34} J·s

Elementary charge(e) = 1.602×10^{-19}C

Vacuum permittivity (ε_0)= $8.854\times10^{-12}\mathrm{J^{-1}\cdot C^2 m^{-1}}$

Electron mass(m_e) = 9.109×10^{-31}kg

Speed of light in vacuum(c) = 2.998×10^{8}m/s

Rydberg constant = $3.29 \text{ x } 10^{15}$ /s^1

$R = 8.314\ \mathrm{J\ mol^{-1}}\ K^{-1} = 0.082\ \mathrm{atm\ L\ mol^{-1}}\ K^{-1}$

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

Raoult's law: vapor pressure of the solvent $P_1 = X_1 P_1^\circ$

Henry's law: vapor pressure of the solute $P_2 = X_2 k_2$

Mole fraction: $X_i = n_i/n_{tot}$ where n_i is the number of moles of component i

Molarity: M = moles of solute per liter of solution ıts

Molality: m = moles of solute per kg of solvent

For *dilute, aqueous* solutions $m \approx$ M

$\Delta U = q + w$. The internal energy of a system is a state function.

$$\Delta H^\circ = \sum_{i-1}^{prod} n_i \Delta H_i^\circ - \sum_{j-1}^{react} n_j \Delta H_j^\circ$$

Gibbs free energy, $G = H - TS$

Isothermal processes: $dw = -PdV$

Heat capacities of ideal monatomic gases

$$c_V \text{ (ideal gas)} = (3/2)\,R$$

$$c_P = c_V + R = (5/2)R$$

$$Z = \frac{V_\mathrm{m}}{V_\mathrm{m}^\mathrm{ideal}} = \frac{V_\mathrm{m}}{RT/P} = \frac{PV_\mathrm{m}}{RT}$$

$$\Delta S = \int_\mathrm{i}^\mathrm{f} \frac{dq_\mathrm{rev}}{T} \qquad \text{(for all processes)}$$

$$\Delta S = \int_\mathrm{i}^\mathrm{f} \frac{dq_\mathrm{rev}}{T} = \frac{1}{T}\int_\mathrm{i}^\mathrm{f} dq_\mathrm{rev} = \frac{q_\mathrm{rev}}{T} \qquad \text{(constant } T\text{)}$$

$$\Delta S_\mathrm{trans} = \frac{q_\mathrm{rev}}{T_\mathrm{trans}} = \frac{\Delta H_\mathrm{trans}}{T_\mathrm{trans}} \qquad \text{(reversible phase transitions at constant } T \text{ and } P\text{)}$$

$$\Delta S = nR\ln\left(\frac{V_2}{V_1}\right) \qquad \text{(ideal gas, change of } V \text{ at constant } T\text{)}$$

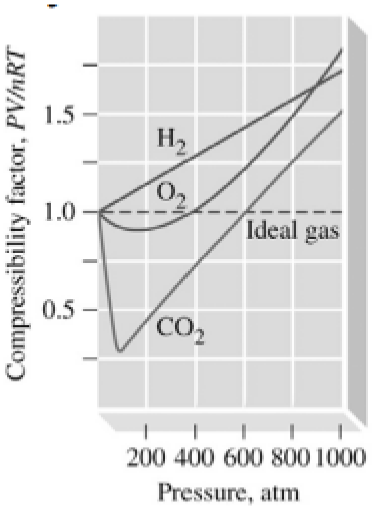
$$\Delta S = \int_{T_1}^{T_2} \frac{nc_V}{T}\,dT = nc_V\ln\left(\frac{T_2}{T_1}\right) \qquad \text{(constant } V \text{ and constant } c_V\text{)}$$

$$\Delta S = \int_{T_1}^{T_2} \frac{nc_P}{T}\,dT = nc_P\ln\left(\frac{T_2}{T_1}\right) \qquad \text{(constant } P \text{ and constant } c_P\text{)}$$

$$\Delta S_\mathrm{surr} = \frac{-\Delta H_\mathrm{sys}}{T_\mathrm{surr}} \qquad \text{(surroundings are a large “heat bath” and pressure of the system is constant)}$$

$$\Delta S_\mathrm{tot} = \Delta S_\mathrm{sys} + \Delta S_\mathrm{surr} > 0 \qquad \text{(spontaneous process)}$$

1. (Total 9 pts) Interpret the deviations of real gas and ideal gas in the following graph about the compressibility factor, Z.



a) (3 pts) Why does Z of H_2 increase as pressure gets higher? (3 pts. No partial pts).

-------------------------------Answer----------------------------------

As pressure gets higher, the volume of molecules of real gases become more unnegligible, and real gas with the same number of molecules of the ideal gas will have larger volume, which results in increase of Z.

Key word : volume of gase molecules

b) (3 pts) Why does Z of O_2 decrease till 200 atm, and then increase again in pressure higher than 200 atm? (3 pts. No partial pts).

-------------------------------Answer----------------------------------

O_2 has larger van der waals force, in other words, stronger attraction to each other compared to H_2, and as a result, becomes a smaller volume compared to ideal gas in the same condition. But as pressure, the effect explained in 1) overwhelms and Z increases.

c) (3 pts) What makes CO_2 have a larger deviation from the ideal gas than O_2? (3 pts. No partial pts).

-------------------------------Answer----------------------------------

CO_2 is heavier, therefore has a larger interaction between molecules due to larger van der waals force.

Keyword : heavy, large interaction

2. (Total 10 pts) Consider a gaseous hydrocarbon at 0.9 atm and 300 K. Upon combusting the entire sample in oxygen (O_2), you will collect a mixture of carbon dioxide (CO_2) and water vapor (H_2O) at 1.8 atm and 360 K. The density of this mixture is 1.80 g/L and the mixture occupies a volume four times as large as that of the pure hydrocarbon. Determine the molecular formula of the hydrocarbon. Assume volume of pure hydrocarbon is 1.00 L. When you write final answer, be careful to raise decimals to the next whole number. (10 pts for correct procedure and correct answer, 5 pts for correct procedure, 0 pt otherwise)

-------------------------------Answer----------------------------------

The volume of products will be 4.00 L

And the mass of products (H_2O+CO_2) will be

1.80 g/L X 4.00 L = 7.2 g products

Assume that hydrocarbon formula is C_xH_y

$$\text{mol of } C_xH_y = n_{C_xH_y} = \frac{PV}{RT} = \frac{0.9\, atm\ \times 1.00\, L}{0.082\, atm \cdot L\,/K \cdot mol \times 300\, K} = 0.0366\, moles$$

$$\text{mol of } product = n_{\text{product}} = \frac{PV}{RT} = \frac{1.8\, atm\ \times 4.00\, L}{0.082\, atm \cdot L\,/K \cdot mol \times 360\, K} = 0.244\, moles$$

Reaction equation is

$$C_xH_y + oxygen \rightarrow xCO_2 + \tfrac{y}{2}H_2O,$$

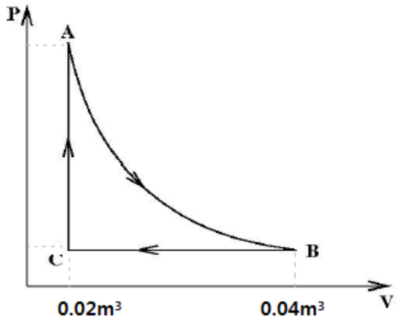
So setting two equation

$$0.0366\text{x mol} + 0.0366 \times \frac{y}{2} mol = 0.244 moles \cdots\cdots\ moles\ of\ products$$

$$\left\{0.0366\text{x mol} \times \left(\frac{44\text{ g}}{\text{mol}}\right)\right\} + \left\{(0.0366 \times \frac{y}{2}\ mol) \times \left(\frac{18\ g}{mol}\right)\right\} = 7.2\ g \cdots\cdots mass\ \ of\ products$$

Solving x=2.9508→ 3, y=7.431→7 (반올림)
So formula is C_3H_7

3. (Total 15 pts) Four moles of monatomic ideal gas goes through the cycle represented in following figure. Process A→B is an isothermal expansion with temperature T_A=300K.



a) (6 pts) Calculate P_A, P_B, and T_c, the pressures and temperature reached in A,B and C. (2 pts each. No partial pts).

------------------------------Answer---------------------------------

Process A→B is isothermal, so T_A=T_B

$$P_A = \frac{nRT_A}{V_A} = \frac{4moles \times (\frac{8.314J}{K \cdot mol}) \times 300K}{0.02m^3} = 4.988 \times \frac{10^5 J}{m^3} = 4.988 \times 10^5 Pa (4.92atm)$$

$$P_B = \frac{nRT_B}{V_B} = \frac{4moles \times (\frac{8.314J}{K \cdot mol}) \times 300K}{0.04m^3} = 2.494 \times 10^5 J/m^3 = 2.494 \times 10^5 Pa (2.46atm)$$

And P_c=P_B and V_C=$V_{A,}$

So

$$T_c = \frac{P_C V_C}{nR} = \frac{P_B V_A}{nR} = \frac{(2.494 \times 10^5 Pa) \times (0.02m^3)}{4moles \times (\frac{8.314J}{K \cdot mol})} = \frac{150 Pa \cdot m^3}{J/K} = 150K$$

b) (9 pts) Fill the following table with numerical values in Joules. (1 pts each. No partial pts).

Process	**△U**	**q**	**w**
A→B			
B→C			
C→A			

-----------------------------Answer----------------------

Process	**△U**	**q**	**w**
A→B	**0**	**6915J**	**-6915J**
B→C	**-7482.6J**	**-12468.6J**	**4986J**
C→A	**7482.6J**	**7482.6J**	**0**

1) A→B

   Because of A→B Process is isothermal, $\triangle U_{AB}=0$

   So ,

   $\Delta U_{AB} = q + w = 0$

   $\mathrm{dg} = -\mathrm{w} = \mathrm{P} \cdot \mathrm{dV} = \left(\frac{nRT}{V}\right) \mathrm{dV}$

   Then integrate V_A to $V_{B,}$

   $\mathrm{q} = 4\mathrm{moles} \times \frac{8.314\mathrm{J}}{\mathrm{K} \cdot \mathrm{mol}} \times 300K \times \ln\frac{0.04}{0.02} = 6915.390791 \ldots J$

   and work is equal to –q, so w=-6915.390791J

2) B→C

   $w_{BC} = -\mathrm{P} \cdot \mathrm{dV} = -(2.493 \times 10^5 Pa) \times (0.02m^3 - 0.04m^3) = 4986J$

   $\Delta U_{BC} = \frac{3}{2} nR\Delta T = \frac{3}{2} \times 4moles \times \frac{8.314J}{K \cdot mol} \times (150K - 300K) = -7482.6J$

   Work is sum of work and heat. So heat(q) = (-7482.6J)-(4986J) = -12468.6J

3) C→A

   Because of $V_A=V_C$ in C→A Process, $w_{CA} = -P \cdot dV = 0$

   So,

   $\mathrm{q} = \Delta U_{CA} = \frac{3}{2} nR\Delta T = \frac{3}{2} \times 4moles \times \frac{8.314J}{K \cdot mol} \times (300K - 150K) = 7482.6J$

4. (Total 15 pts) Answer the following questions.

a) (5 pts) Phase changes occur between different solid forms, as well as from solid to liquid, liquid to gas, and solid to gas. When white tin at 1.00 atm is cooled below 13.2 ℃, it spontaneously changes (over a period of weeks) to gray tin. The density of gray tin is less than the density of white tin (5.75 g cm^{-3} vs 7.31 g cm^{-3}). Some white tin is compressed to a pressure of 2.00 atm. At this pressure, should the temperature be higher or lower than 13.2 ℃ for the conversion to gray tin to occur? Explain your reasoning. (5 pts for perfect answer, 3 pts for mediocre answer, 0 pts otherwise).

-----------------------------Answer----------------------

Gray tin is favored over white tin by lower temperature, but white tin is favored by higher pressure (because it is more dense than gray tin). Suppose the two forms of tin are present at equilibrium at 1 atm and 13.2 ℃. Raising the pressure to 2 atm (eventually) converts all of the tin to white tin. In order to restore the gray allotrope the temperature must be adjusted in the direction that favors gray tin, that is, the temperature must be lowered below 13.2 ℃

b) (5 pts) List the following substances in order of increasing normal boiling points, T_b, and explain your reasoning. : He, HF, NO, NH_4Cl, Ne (5 pts for correct order and reasons. 3 pts for correct order. 0 pts otherwise).

-----------------------------Answer----------------------

He < Ne (more heavy) < NO (weak dipole-dipole interaction) < HF(strong dipole-dipole interaction, i.e. hydrogen-bonding) < NH_4Cl (ionic interaction)

c) (5 pts) Below are the Van der Waals constant for three unknown gases. If the Three gases are SO_2, CO_2, and H_2O, Identify this gases as A, B, or C and give brief reasons. (5 pt for correct matching and reasoning. No partial pts).

	a (atm·L^2/mol^2)	b (L/mol)
A	3.59	0.0427
B	5.46	0.0305
C	6.71	0.0564

------------------------------Answer----------------------

A - CO_2 : nonpolar molecule.

So smallest value of constant a

B - H_2O : because this is polar molecule, high value of constant a. But size is smaller than SO_2.

So smaller value of constant b.

C - SO_2 : This molecule is polar molecules and have the bigger size.

So high values of constant a and b

5. (Total 14 pts) Imagine that two 1 L beakers, A and B, each containing an aqueous solution of fructose (a nonvolatile sugar with molecular weight = 180) are placed together in a box, which is then sealed. (The concentrations of the solutions are not necessarily the same.) The temperature remains constant at 26 ℃. Initially, there is 500 mL of solution in A and 100 mL of solution in B. As the solutions stand in the sealed box, their volumes change slowly for a while. When they stop changing, beaker A contains 300 mL and beaker B contains 300 mL. It is then determined that the solution in A is 1.0 M in fructose and has a density of 1.10 g mL^{-1}.

a) (5 pts) What is the molar concentration of fructose in the solution in beaker B at the end? Explain. (5 pts correct procedure and answer. 3 pts for correct procedure. 0 pt otherwsie).

------------------------------Answer-----------------------

At equilibrium, the partial pressure of H_2O above beaker A equals the partial pressure of water above beaker B. Obviously, the mole fractions of fructose and H_2O add up to 1 in both beakers. Moreover, the mole fractions of fructose in the two beakers are equal, as the following confirms

$$P_{H2O,A} = P_{H2O,B}$$

$$(X_{H2O,A})P'_{H2O} = (X_{H2O,B})P'_{H2O}$$

$$(1 - X_{fructose,A})P'_{H2O} = (1 - X_{fructose,B})P'_{H2O}$$

$$(1 - X_{fructose,A}) = (1 - X_{fructose,B})$$

$$(X_{fructose,A}) = (X_{fructose,B}) \text{ at equilibrium}$$

Abbreviate fructose with the letter f. Then $[f]_A$ and $[f]_B$ represent the molar concentrations of fructose in beakers A and B respectively. It was just shown that $X_{f,A} = X_{f,B}$. Therefore at the end

$[f]_A$ = $[f]_B$ = 1.0 mol L-1

b) (3 pts) Calculate the concentration of fructose in the solution in A at the start. (3 pts. No partial pts).

------------------------------Answer-----------------------

The amount of fructose in each beaker is unchanged throughout. Hence

$$[f]_{initial,A} = [f]_{final,A}\left(\frac{V_{final,A}}{V_{initial,A}}\right) = (1.0\ mol\ L^{-1})\frac{300\ mL}{500\ mL} = 0.6\ mol\ L^{-1}$$

c) (3 pts) Calculate the concentration of the fructose in the solution in B at the start. (3 pts. No partial pts).

------------------------------Answer-----------------------

Similarly for beaker B

$$[f]_{initial,B} = [f]_{final,B}\left(\frac{V_{final,B}}{V_{initial,B}}\right) = (1.0\ mol\ L^{-1})\frac{300\ mL}{100\ mL} = 3.0\ mol\ L^{-1}$$

d) (3 pts) The vapor pressure of pure water at 26 ℃ is 25.2 torr. What is the pressure of water vapor in the box at the end, after the volumes have stopped changing? (3 pts. No partial pts).

------------------------------Answer-----------------------

The total volume of solution does not matter for this part. Assume 1000 mL for simplicity. The mass of the solution is then 1100 g, and the mass of the solute (fructose) in the solution is 1.0 mol L^{-1} X 180 g mol^{-1} = 180 g. Then

$$n_{H2O} = \frac{m_{H2O}}{M} = \frac{m_{solution} - m_{solute}}{M} = \frac{(1100 - 180)}{18.0\ g\ mol^{-1}} = 51.1\ mol$$

$$X_{H2O} = \frac{n_{H2O}}{n_{H2O} + n_{fructose}} = \frac{51.1\ mol}{51.1\ mol + 1.0\ mol}$$

$$P_{H2O} = X_{H2O}P°_{H2O}$$

$$P_{H2O} = \left(\frac{51.1\ mol}{(1.0 + 51.1)mol}\right)25.2\ torr = 24.7\ torr$$

6. (Total 15 pts) Answer the following questions.

a) (5 pts) Complete and balance the following equations for reactions taking place in basic solution. (5 pts. No partial pts).

$$Ag(s) + HS^{-}(aq) + CrO_4^{2-}(aq) \rightarrow Ag_2S(s) + Cr(OH)_3\ (s)$$

--------------------Answer--

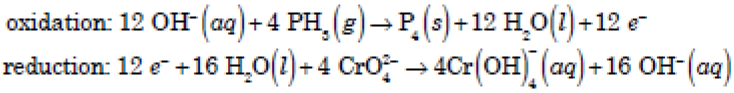
a) $6\ Ag(s) + 3\ HS^{-}(aq) + 2\ CrO_4^{2-}(aq) + 5\ H_2O(aq) \rightarrow 3\ Ag_2S(s) + 2\ Cr(OH)_3\ (s) + 7\ OH^{-}$

b) (5 pts) The following balanced equations represent reactions that occur in aqueous acid or base. Break them down into balanced oxidation and reduction half-equations. (5 pts. No partial pts).

$$4PH_3(g) + 4H_2O(l) + 4CrO_4^{2-}(aq) \rightarrow P_4(s) + 4Cr(OH)_4^-(aq) + 4OH^-(aq)$$

--------------------Answer---------------------------------------

b)



oxidation: $12\ OH^-(aq) + 4\ PH_3(g) \rightarrow P_4(s) + 12\ H_2O(l) + 12\ e^-$

reduction: $12\ e^- + 16\ H_2O(l) + 4\ CrO_4^{2-} \rightarrow 4Cr(OH)_4^-(aq) + 16\ OH^-(aq)$

c) (Total 5 pts) A mixture of benzene and toluene contains benzene of mole fraction 0.4. When this solution is at equilibrium with vapor phase at 30 ℃, calculate the mole fraction of benzene in the vapor phase. At 30 ℃, the vapor pressure of benzene and toluene are 120 torr and 40 torr, respectively. (5 pts for correct procedure and answer. No partial pts).

--------------------Answer--

$P_T = X_T P^o_T$, $P_B = X_B P^o_B$

$P_{total} = P_T + P_B = X_A P^o_A + X_B P^o_B$

$P_B = X_B P^o_B = 0.4 \times 120 = 48$ torr

$P_T = X_T P^o_T = 0.6 \times 40 = 24$ torr

$X_B = \frac{48 torr}{(48+24) torr} = 0.67$

7. (Total 13 pts) A sample of pure solid naphthalene ($\mathrm{C_{10}H_8}$) weighing 0.6410g is burned completely with oxygen to $\mathrm{CO_2}$(g) and $\mathrm{H_2O}$(l) in a constant-volume calorimeter at 25 ℃. The amount of heat evolved is observed to be 25.79 kJ.

a) (3 pts) Write and balance the chemical equation for the combustion reaction. (3 pts. No partial pts).

--------------------Answer--

The equation is $C_{10}H_8(s) + 12\ O_2(g) \rightarrow 10\ CO_2(g) + 4H_2O(l)$

b) (10 pts) Calculate the standard change in internal energy (ΔU°) and the standard enthalpy change (ΔH°) for the combustion for the 1.000 mol naphthalene to CO_2(g) and H_2O(l). (5 pts each. No partial pts).

--------------------Answer---------------------------------------

The amount of heat evolved (-q) in the combustion of 0.6410 g of naphthalene was observed to equal 25.79 kJ. Since the combustion was performed at constant volume, no work was done on the system (w=0). Therefore, $\Delta U = q + w = -25.79\ kJ + 0 = -25.79\ kJ$. Put this ΔU on a molar basis to correspond to the 1 mol of naphthalene appearing in the balanced equation

$$\Delta U = \left(\frac{-25.79\ kJ}{0.6410\ g\ C_{10}H_8}\right) \times \left(\frac{128.17\ g\ C_{10}H_8}{1\ mol\ C_{10}H_8}\right) = -5157\ kJ\ mol^{-1}$$

The temperature is 25 ℃ both before and after the reaction. Therefore for the equation written above (which shows 1 mol of naphthalene) $\Delta U° = -5157\ kJ\ mol^{-1}$

To calculate $\Delta H°$ use the definition

$$\Delta H° = \Delta U° + \Delta(PV)$$

Assume that the gases are ideal and that the volumes of the solids are negligible. Then $\Delta(PV) = (\Delta n_g)RT$, and

$$\Delta H° = \Delta U° + (\Delta n_g)RT$$

The Δn_g is the change in the number of moles of gases during the reaction. The combustion of 1 mol of naphthalene produces 10 mol of gas, while consuming 12 mol of gas. Accordingly

$$(\Delta n_g)RT = (-2\ mol)(8.3145\ J\ K^{-1}\ mol^{-1})(298.15\ K) = -4.96\ kJ$$

$$\Delta H° = \Delta U° + (\Delta n_g)RT = -5157\ kJ - 4.96\ kJ = -5162\ kJ$$

8. (Total 12 pts) Initially a sample of ideal gas at 323 K occupies 1.67 L at 4.95 atm. The gas is allowed to expand to 7.33 L by to pathways: (i) isothermal, reversible expansion; (ii) isothermal, irreversible free expansion.

a) (3 pts) Calculate ΔS_{tot}, ΔS, and ΔS_{surr} for isothermal, reversible expansion. (3 pts for correct procedure and answer. No partial pts).

--------------------Answer---------------------------------------

The moles of ideal gas : n

$$n = \frac{PV}{RT} = \frac{(4.95\ \mathrm{atm}) \times (1.67\ \mathrm{L})}{(0.082\ \mathrm{atm \cdot L \cdot mol^{-1} \cdot K^{-1}}) \times (323\ \mathrm{K})} = 0.31\ \mathrm{mol}$$

Isothermal, reversible expansion

$$\Delta S = nR \cdot \ln\frac{V_2}{V_1}$$

$$= (0.31\ \mathrm{mol}) \times (8.3145\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}}) \times \ln\frac{(7.33\ \mathrm{L})}{(1.67\ \mathrm{L})} = 3.81\ \mathrm{J \cdot K^{-1}}$$

$$w_{rev} = -nRT \cdot \ln\frac{V_2}{V_1} \Rightarrow q_{rev} = -w_{rev} \Rightarrow q_{surr} = -q_{rev} = w_{rev} = -nRT \cdot \ln\frac{V_2}{V_1}$$

$$\Delta S_{surr} = \frac{q_{surr}}{T}$$

$$= -nR \cdot \ln\frac{V_2}{V_1} = -(0.31\ \mathrm{mol}) \times (8.3145\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}}) \times \ln\frac{(7.33\ \mathrm{L})}{(1.67\ \mathrm{L})} = 3.81\ \mathrm{J \cdot K^{-1}}$$

$$\therefore \Delta S_{tot} = \Delta S + \Delta S_{surr} = 0$$

b) (3 pts) Calculate ΔS_{tot}, ΔS, and ΔS_{surr} for isothermal, irreversible free expansion. (3 pts for correct procedure and answer. No partial pts).

--------------------Answer--

Isothermal, irreversible expansion

$$\Delta S = nR \cdot \ln\frac{V_2}{V_1}$$
$$= (0.31\ \mathrm{mol}) \times (8.3145\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}}) \times \ln\frac{(7.33\ \mathrm{L})}{(1.67\ \mathrm{L})} = 3.81\ \mathrm{J \cdot K^{-1}}$$

$$P_{ext} = 0 \Rightarrow w_{irrev} = 0 \Rightarrow q_{irrev} = -w_{irrev} \Rightarrow q_{surr} = -q_{irrev} = w_{irrev} = 0$$

$\Delta S_{surr} = \frac{q_{surr}}{T} = 0$

$\therefore \Delta S_{tot} = \Delta S + \Delta S_{surr} = 3.81\ \mathrm{J \cdot K^{-1}} > 0$

c) (3 pts) Calculate the work for irreversible expansion against a constant external pressure. (3 pts for correct procedure and answer. No partial pts).

--------------------Answer---------------------------------------

The irreversible work of expansion against a constant opposing pressure is given by

$w = -P_{ex}\,\Delta V = -(4.95\ \text{atm})(7.33\ \text{L} - 4.95\ \text{L})$

$= -11.78\ \text{L atm} = -1193.61\ \text{J}$ (1 L atm = 101.325 J/L atm)

d) (3 pts) Calculate the work for isothermal, reversible expansion. (3 pts for correct procedure and answer. No partial pts).

--------------------Answer---------------------------------------

An isothermal expansion will be given by

$w = -nRT\ \ln(V_2/V_1)$

n is calculated from the ideal gas law

$n = PV/RT = (4.95\ \text{atm})(1.67\ \text{L})/(0.082\ \text{L atm/K mol})(323\ \text{K}) = 0.31\ \text{mol}$

$w = -(0.31\ \text{mol})(8.314\ \text{J/K mol})(323\ \text{K})\ \ln(7.33/4.95) = -326.82\ \text{J}$

9. (Total 17 pts) Answer the following questions.

a) (3 pts) Calculate the change in molar Gibbs free energy for the process $\mathrm{Hg}(l) \rightarrow \mathrm{Hg}(s)$ at 1 atm and 350 ℃. The enthalpy of vaporization is 59.3 kJ·mol^{-1}, and the entropy of vaporization is 94.2 $\mathrm{J} \cdot K^{-1}$ ·mol^{-1}. In each case, indicate whether or not vaporization would be spontaneous. (3 pts for correct procedure and answer. No partial pts).

--------------------Answer--

$\Delta G° = \Delta H° - T\Delta S° = (59.3\ \mathrm{kJ\ mol^{-1}}) - (623\ \mathrm{K})(0.0942\ \mathrm{kJ\ K^{-1}\ mol^{-1}}) = 0.6\ \mathrm{kJ\ mol^{-1}}$

So this reaction is not spontaneous

b) (3 pts) Estimate T at which it is thermodynamically possible under standard conditions. (3 pts for correct procedure and answer. No partial pts).

--------------------Answer--

$\Delta G° = \Delta H° - T\Delta S° = 59.3\ \mathrm{kJ\ mol^{-1}} - T \times (0.0942\ \mathrm{kJ\ K^{-1}\ mol^{-1}}) = 0$

T = 629.51 K (= 356.36 ℃)

c) (Total 5 pts) At 298 K chlorine is only slightly soluble in water. Thus, under a pressure of 1.00 atm of $Cl_2(g)$, 1.00 L of water at equilibrium dissolves just 0.091 mol of Cl_2.

$$Cl_2(g) \rightleftharpoons Cl_2(aq)$$

In such solutions the $Cl_2(aq)$ concentration is 0.061 M and the concentrations of $Cl^-(aq)$ and HOCl(*aq*) are both 0.030 M. These two additional species are formed by the equilibrium

$$Cl_2(aq) + H_2O(l) \rightleftharpoons H^+(aq) + Cl^-(aq) + HOCl(aq)$$

There are no other Cl-containing species. Compute the equilibrium constants *K*1 and *K*2 for the two reactions. (5 pts for correct procedure and correct answer, 1.5 pts for one correct answer, 1 pts for one correct procedure, 0 pt otherwise)

--------------------Answer---------------------------------------

The first equation and its mass-action expression are

$$Cl_2(g) \rightleftharpoons Cl_2(aq), \frac{[Cl_2]}{P_{Cl_2}} = \mathrm{K}$$

Take the equilibrium concentrations of the dissolved chlorine and the partial pressure of the gaseous chlorine from the statement of the problem

$$K_1 = \frac{[Cl_2]}{P_{Cl_2}} = \frac{0.061}{1.00} = 0.061$$

The second reaction and its mass-action expression are

$$Cl_2(aq) + H_2O(l) \rightleftharpoons H^+(aq) + Cl^-(aq) + HOCl(aq), \frac{[HOCl][H^+][Cl^-]}{[Cl_2]} = K_2$$

K2 is readily calculated because [H+] must be equal to [Cl-] and to [HOCl], based on the 1-to-1-to-1 stoichiometry of the reaction

$$K_2 = \frac{[HOCl][H^+][Cl^-]}{[Cl_2]} = \frac{(0.030)(0.030)(0.030)}{(0.061)} = 4.4 \times 10^{-4}$$

d) (Total 6 pts) When 1.00 g potassium chlorate ($KClO_3$) is dissolved in 50.0 g water in a Styrofoam calorimeter of negligible heat capacity, the temperature decreases from 25.00 ℃ to 23.36 ℃. Calculate q for the water and ΔH° for the process.

$$KClO_3(s) \rightarrow K^+(aq) + ClO_3^-(aq)$$

The specific heat of water is 4.184 J K^{-1} g^{-1}. The molar mass of $KClO_3(s)$ is 122.55 g. (3 pts each. No partial pts).

--------------------Answer---------------------------------------

$$q_{\mathrm{water}} = (50.0\,g)(4.184\,J\,K^{-1}\,g^{-1})(23.36 - 25.00\,K) = -343\,J$$

$$\Delta\mathrm{H}° = \left(\frac{343\,J}{1\,g\,KClO_3}\right)\left(\frac{122.55\,g\,KClO_3}{1\,mol\,KClO_3}\right) = 4.2\ \times 10^4\mathrm{J} = 42\ \mathrm{kJ}$$

10. (Total 12 pts) There are two isomeric hydrocarbons with formula C_4H_{10}, butane and isobutene, which we denote here B and I. The standard enthalpies of formation for the gaseous species are -124.7 kJ/mol for B, -131.3 kJ/mol for I. The standard free energies of formation are -15.9 kJ/mol for B, -18.0 kJ/mol for I.

a) (6 pts) Which is the more stable under standard conditions, and which has the higher entropy? (6 pts for correct procedure and correct answer, 3 pts for correct procedure, 0 pt otherwise)

--------------------Answer--

The reaction is the isomerization of butane to isobutene, $\mathrm{B} \rightarrow \mathrm{I}$.

Then, $\Delta \mathrm{G_f}°(I) = -18 - (-15.9)\, kJ = -2.1\, kJ$

The means that isobutene is more stable than butane (at 298 K and 1 atm),

$$\Delta \mathrm{G_f}° = \Delta H_f° - T\Delta S_f° : \Delta S_f° = \frac{1}{T}(\Delta H_f° - \Delta G_f°)$$

$$\Delta \mathrm{S_f}°(B) = \frac{-124.6 - (-15.9)}{298.15\, K} \times 10^3\, J\, mol^{-1} = -365\, J\, K^{-1}\, mol^{-1}$$

$$\Delta \mathrm{S_f}°(I) = \frac{-131.3 - (-18.0)}{298.15\, K} \times 10^3\, J\, mol^{-1} = -380\, J\, K^{-1}\, mol^{-1}$$

Butane has a higher (more positive) entropy than isobutene.

b) (6 pts) The reaction B $\rightleftharpoons$ I can occur in the presence of a catalyst. Calculate the equilibrium constant at 298 K for the conversion of B to I, and calculate the percentage of B in the equilibrium mixture. (6 pts for correct procedure and correct answer, 3 pts for correct procedure, 0 pt otherwise)

--------------------Answer---------------------------------------

$$\ln K = \frac{\Delta G°}{-RT} = \frac{2.1 \times 10^3\, J\, mol^{-1}}{(8.31\, J\, K^{-1} mol^{-1})298\, K} = 0.85\,, K = 2.3$$

Let X be the fraction of B. Then (1-X) is the fraction of I.

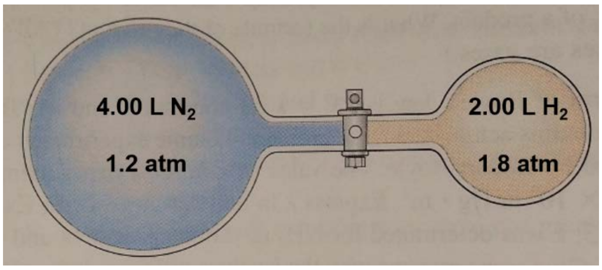
Then, $\mathrm{K} = \frac{1-X}{X} = 2.3,\ \ 2.3X = 1 - X,\ X = \frac{1}{3.3} = 0.30$

The percentage of B in the equilibrium mixture is therefore 30 %.

11. (Total 24 pts) The reaction between nitrogen and hydrogen to produce ammonia.

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

Assume this reaction is carried out in the containers illustrated below.



The stopcock between the two containers is opened, and the reaction proceeds. The final container volume is 6.00L, the temperature is 400 ℃ constantly. Use the following data if necessary.

Substance	$\Delta H_f°$ (400 ℃) kJ mol^{-1}	$\Delta S°$ (400 ℃) J K^{-1} mol^{-1}
N_2	0	191.50
H_2	0	130.57
NH_3	-46.11	192.34

1) (8 pts) Calculate the partial pressure of NH_3 after equilibrium is reached at this temperature. (8 pts for correct procedure and answer. 4 pts for correct procedure. Otherwise no partial pts).

--------------------answer--

For N_2 : $P_{after} = \frac{P_{initial}V_{initial}}{V_{after}} = 1.2atm \times \frac{4.00L}{6.00L} = 0.8atm$

For H_2 : $P_{after} = \frac{P_{initial}V_{initial}}{V_{after}} = 1.8atm \times \frac{2.00L}{6.00L} = 0.6atm$

$\Delta H° = 2\ \Delta H_f°(NH_3) = -92.22$ kJ

$\Delta S° = 2\ \Delta S°(NH_3) - 3\ \Delta S°(H_2) - \Delta S°(N_2) = -198.53$ J K-1

$\Delta G° = \Delta H° - T\Delta S° = -92220\ J\ mol^{-1} - (673\ K)(-198.53\ J\ K^{-1}\ mol^{-1})$

$= 41390\ J\ mol^{-1} = 41.39\ kJ\ mol^{-1}$

$\Delta G° = -RT\ln K$ ➔ $K = e^{-\Delta G°/RT} = 6.13 \times 10^{-4}$

N_2	3 H_2	⇌	2 NH_3
0.8	0.6		
-x	-3x		+2x
(0.8-x)	(0.6-3x)		2x

K = $\frac{(2x^2)}{(0.8-x)(0.6-3x)^3}$ = 6.13 x 10^{-4}, so, x = 4.94 x 10^{-3}

∴ P_{NH3} = 2 x 4.94 x 10^{-3} = 9.88 x 10^{-3} atm

b) (6 pts) Calculate ΔS_{sys}. (6 pts for correct procedure and answer. 3 pts for correct procedure. 0 pts otherwise).

--------------------answer---------------------------------------

$\Delta S_{sys} = \Delta S_{N2\ expansion} + \Delta S_{H2\ expansion} + \Delta S_{reaction}$

$$\mathrm{n_{N2}} = \frac{PV}{RT} = \frac{(1.2\ atm)(4.0\ L)}{(0.082\ atm\ L\ mol^{-1}\ K^{-1})(673\ K)} = 0.087\ mol$$

$$\mathrm{n_{H2}} = \frac{PV}{RT} = \frac{(1.8\ atm)(2.0\ L)}{(0.082\ atm\ L\ mol^{-1}\ K^{-1})(673\ K)} = 0.065\ mol$$

$\Delta S_{N2\ expansion}$ = nR $\ln(\frac{V_2}{V_1})$ = $(0.087\ \mathrm{mol})(8.314\ J\ K^{-1}mol^{-1})\ln(\frac{6\ L}{4\ L}) = 0.293\ J\ K^{-1}$

$\Delta S_{H2\ expansion}$ = nR $\ln(\frac{V_2}{V_1})$ = $(0.065\ \mathrm{mol})(8.314\ J\ K^{-1}mol^{-1})\ln(\frac{6\ L}{2\ L}) = 0.594\ J\ K^{-1}$

$\Delta S_{reaction} = \Delta S° = 2\ \Delta S°(NH_3) - 3\ \Delta S°(H_2) - \Delta S°(N_2) = -198.53\ J\ K^{-1}$

So, $\Delta S_{sys} = -197.643\ J\ K^{-1}$

c) (6 pts) Calculate ΔS_{surr}. (6 pts for correct procedure and answer. 3 pts for correct procedure. 0 pts otherwise).

--------------------answer--

If this reaction is isothermal, reversible expansion, $\Delta S_{tot} = \Delta S + \Delta S_{surr} = 0$

$$\Delta S_{surr} = 197.643\,\mathrm{J \cdot K^{-1}}$$

If isothermal, irreversible expansion,

$$P_{ext} = 0 \Rightarrow w_{irrev} = 0 \Rightarrow q_{irrev} = -w_{irrev} \Rightarrow q_{surr} = -q_{irrev} = w_{irrev} = 0$$

$$\Delta S_{surr} = \frac{q_{surr}}{T} = 0$$

As we don't know this reaction is reversible expansion or irreversible expansion, we can assume that ΔS_{surr} would be somewhere between 0 and~~∼~~ 197.643 J K^{-1}

d) (4 pts) The reaction is allowed to reach equilibrium at 400 ℃. Certain changes are then made to this mixture. Considering each change separately, state the effect (increase, decrease, or not change) that the change has on the original equilibrium values of the quantity in the second column. The temperature and volume are constant. (1 pts each. No partial pts).

Change	Quantity	Change
Add H_2	Amount of NH_3	
Remove H_2	Amount of NH_3	
Remove H_2	Amount of N_2	
Add NH_3	*K*	

--------------------answer---------------------------------------

Increases / Decreases / Increases / No change