

[1] (10 points total)

(a) (3 points) A group of six students took turns weighing a beaker containing a sample of water using the same laboratory balance. The results were:

111.4 g, 111.6 g, 111.2 g, 111.0 g, 111.4 g and 111.3 g.

The teaching assistant then weighed the same beaker of water on a more accurate balance and obtained the value of 105.602 g.

Comment on the degree of precision and the degree of accuracy of the student results.

(b) (4 points) Estimate the volume of a water molecule from the following data. Molar mass of water = 18.0 g mol⁻¹. Density of water = 1.00 g cm⁻³.

(c) (3 points) Calculate the mass of ferric chloride hexahydrate (FeCl₃·6H₂O) that is needed to make 250.0 mL of a 0.020M solution (M = mol L⁻¹). Show working.

[molar masses (g mol⁻¹): H = 1.01; O = 16.00; Cl = 35.45; Fe = 55.85]

Answers)

(a) Mean mass = 111.3 g (± 0.3 g); precision is good but ... accuracy is poor, because 111.3 g differs considerably (~5%) from 105.602 g.

(b) Molar volume = 18.0 g mol⁻¹/1.00 g cm⁻³
= 18.0 cm³ mol⁻¹

Thus, 18.0 cm³ contains 6.02 x 10²³ molecules of water

Hence, the volume per water molecule is 18.0 cm³ mol⁻¹/6.02 x 10²³ mol⁻¹
= 2.99 x 10⁻²³ cm³

This is equivalent to a cube of sides ~3 x 10⁻⁸ cm (3 Å) long.

(c) Molar mass of FeCl₃·6H₂O = 270.32 g/mol

To make 1 L of 0.02 M solution, we need 270.32 x 0.02 g

Hence, 270.32 x 0.02 x (250/1000) is needed to make 250.0 mL of 0.02 M solution

= 1.35 g (3 점)

단위: -1

답만 틀린 계산 실수: -1

(a) precision 의 의미 이해 및 평균계산, 편차계산 : 1 점

accuracy 의 의미 이해 및 error calculation: 1 점

precision good, accuracy poor: 1 점

(b) molar volume = 18.0 cm³ mol⁻¹ : 2 점

water molecule volume = 2.99 x 10⁻²³ cm³ 2 점

단위 틀리면 -1

계산실수 작은 것 답만틀림 -1

(c) Molar mass of FeCl₃·6H₂O = 270.32 g/mol

270.32 x 0.02 x (250/1000) is needed to make 250.0 mL of 0.02 M solution = 1.35 g

1.35 g (3 점)

단위: -1

답만 틀린 계산 실수: -1

6H₂O 빼고 계산한 것 1 점

[2] (10 points total) Light with a wavelength of 525 nm strikes the surface of cesium in a photocell. The work function of cesium is 3.43×10^{-19} J.

(a) (4 points) Calculate the maximum velocity of the photoelectrons.

(b) (3 points) Compute the de Broglie wavelength for the photoelectron in (a).

(c) (3 points) Calculate the longest wavelength of light that is capable of ejecting electrons from the surface of cesium.

Answers)

$$(a) E = hv = \frac{hc}{\lambda} = \frac{(6.63 \times 10^{-34} \text{ Js})(3.00 \times 10^8 \text{ m s}^{-1})}{525 \times 10^{-9} \text{ m}} = 3.79 \times 10^{-19} \text{ J}$$

$$E_k = \frac{1}{2}mv^2 = E - E_0 = (3.79 - 3.43) \times 10^{-19} \text{ J} = 3.6 \times 10^{-20} \text{ J}$$

$$v = \sqrt{\frac{2E_k}{m}} = \sqrt{\frac{2 \times 3.6 \times 10^{-20} \text{ kg m}^2 \text{ s}^{-2}}{9.11 \times 10^{-31} \text{ kg}}} = 2.81 \times 10^5 \text{ m s}^{-1}$$

$$(b) \lambda = \frac{h}{mv} = \frac{6.63 \times 10^{-34} \text{ Js}}{(9.11 \times 10^{-31} \text{ kg})(2.81 \times 10^5 \text{ m s}^{-1})} = 2.59 \times 10^{-9} \text{ m}$$

(a) Equation: 2 points, answer: 2 points, No unit: -1 point

(b) Equation: 2 points, answer: 1 points, No unit: -1 point

(c) The longest wavelength to promote the photoelectric effect for cesium is given by the work function.

$$\begin{aligned} \Phi &= 3.43 \times 10^{-19} \text{ J} \\ &= hv_0 \\ &= hc/\lambda_0 \\ &= \frac{6.626 \times 10^{-34} \text{ J s} \times 3.00 \times 10^8 \text{ m s}^{-1}}{\lambda_0} \\ \lambda_0 &= \frac{6.626 \times 10^{-34} \text{ J s} \times 3.00 \times 10^8 \text{ m s}^{-1}}{3.43 \times 10^{-19} \text{ J}} \\ &= \underline{5.80 \times 10^{-7} \text{ m or 580 nm}} \end{aligned}$$

(c) Equation: 2 points, answer: 1 points, No unit: -1 point

[3] (15 points total) In the following problems, please report your final answers in units of eV or Å.

(a) (5 points) Suppose two electrons and a helium nucleus are arranged in an equilateral triangle that is 2.00 Å on each side. What is the potential energy of either electron?

(b) (5 points) Suggest a better way (a way of lowering the total potential energy) of arranging the electrons that preserves the electron-nucleus distances. What is the total potential energy of the three particles in this case?

(c) (5 points) The general formula for the de Broglie wavelength that accounts for the presence of potential energy is

$$\lambda(r) = \frac{h}{\sqrt{2m[E - V(r)]}}$$

Calculate the deBroglie wavelength in Å for an electron in helium (assume 4.00 amu for the He nucleus) at a fixed total energy E of -3.40 eV at a distance of 2.0 Å from the nucleus. Electron-electron repulsion may be ignored.

Answers)

$$h = 6.626 \times 10^{-34} \text{ J} \cdot \text{s}$$

$$m_e = 9.109 \times 10^{-31} \text{ kg}$$

$$1\text{eV} = 1.602 \times 10^{-19} \text{ J}$$

$$V(\text{eV}) = 14.40 \frac{q_1 q_2}{r}, \text{ where the charges are expressed in units of } e.$$

$$(a) V_e = \frac{(-e)(-e)}{r_{ee}} + \frac{(2e)(-e)}{r_{ne}} = 14.40 \left(\frac{1}{2} - \frac{2}{2} \right) = -7.20 \text{ eV}$$

(-) 없어도 0 점

(b) The potential energy can be decreased by moving the electrons apart; the best we can do is a collinear arrangement $e^- \text{---} \text{He}^{2+} \text{---} e^-$, yielding (2 점)

$$V_e = \frac{(-e)(-e)}{r_{ee}} + 2 \frac{(2e)(-e)}{r_{ne}} = 14.40 \left(\frac{1}{4} - 2 \frac{2}{2} \right) = -25.20 \text{ eV} \text{ (3 점)}$$

(c)

$$V(\text{eV}) = 14.40 \frac{q_1 q_2}{r} = -14.40 \frac{2 \times 1}{2.0} = -14.40 \text{ eV} = -2.31 \times 10^{-18} \text{ J}$$

$$\lambda = \frac{6.626 \times 10^{-34} \text{ J} \cdot \text{s}}{\sqrt{2 \times (9.109 \times 10^{-31} \text{ kg}) \times (-3.40 \times (1.602 \times 10^{-19} \text{ J}) + 2.31 \times 10^{-18} \text{ J})}} = 3.75 \times 10^{-10} \text{ m}$$

3.75 Å (3 점)

$V(\text{eV}) = -2.31 \times 10^{-18} \text{ J}$ (2 점)

[4] (15 points total) Consider the one-electron species H, He⁺, and Li²⁺ in their ground states.

(a) (5 points) Compute the ionization energy for the species that has the smallest radius.

The Rydberg constant is $R = 2.18 \times 10^{-18}$ J/atom (or 1312 kJ/mol)

(b) (5 points) Compute the longest wavelength in the Lyman series (transition to the ground state) for both H and He⁺.

(c) (5 points) Without attempting a detailed calculation, estimate the first ionization energy in terms of kJ/mol for a ground-state helium atom (He). Determine the lowest and highest values possible.

Answers)

(a) H has 1 proton and 1 electron.

He⁺ has 2 protons and 1 electron.

Li²⁺ has 3 protons and 1 electron.

As we go from H to Li²⁺, the Coulomb force between the nucleus and electron increases.

Therefore, **the radius of Li²⁺ is the smallest.** **Li²⁺ 언급하면 2 점**

The ionization energy is the energy to move the electron from $n=1$ to $n=\infty$.

$$\text{Therefore } E_{\infty} - E_1 = -RZ^2 \left(\frac{1}{\infty^2} - \frac{1}{1^2} \right) = RZ^2$$

$e^2 Z^2 / 2a_0$ (a_0 값 언급), $Z^2 hc R_H$ (R_H 값 언급) 2 점

$$\text{H}(Z=1) \quad R \quad 2.18 \times 10^{-17} \text{J}$$

$$\text{He}^+(Z=2) \quad 4R \quad 8.72 \times 10^{-17} \text{J}$$

$$\text{Li}^{2+}(Z=3) \quad 9R \quad 1.96 \times 10^{-16} \text{J} \quad (\text{답만 맞으면 1 점})$$

(b) Lyman series corresponds to the line spectra from the transition from an initial state (n_i) to the final state (n_f) of 1s ground state. The longest wavelength is from $n_i=2$ to $n_f=1$.

$$\Delta E = -RZ^2\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) = -RZ^2\left(1 - \frac{1}{4}\right) = -\frac{3}{4}RZ^2$$

$$\Delta E = h\nu = \frac{hc}{\lambda},$$

$$\frac{hc}{\lambda} = \frac{3}{4}RZ^2$$

$$\lambda = \frac{4hc}{3RZ^2} = \frac{4 \times (6.63 \times 10^{-34} \text{ Js})(3.00 \times 10^8 \text{ ms}^{-1})}{3 \times (2.18 \times 10^{-18} \text{ J})Z^2}$$

$$= 1.217 \times 10^{-7} \text{ m} / Z^2 = 121.7 \text{ nm} / Z^2$$

equation 3 점

For H(Z=1), the wavelength is 121.7nm (122nm) (1 점) and for He⁺(Z=2), 30.4 nm.

(1 점)

(c) $E_\infty - E_1 = RZ^2$ or the screening effect (1 점)

In the Helium atom, 2 1s² electrons are attracted to 2 protons (Z = 2). Here we need to consider the screening effect of electrons. Therefore, we have to consider two extreme cases for the screening effect and their Z_{eff}. Then using the above equation, we can estimate the maximum and minimum ionization energies.

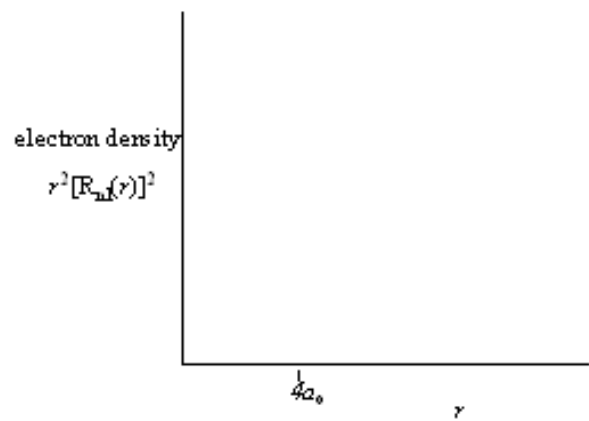
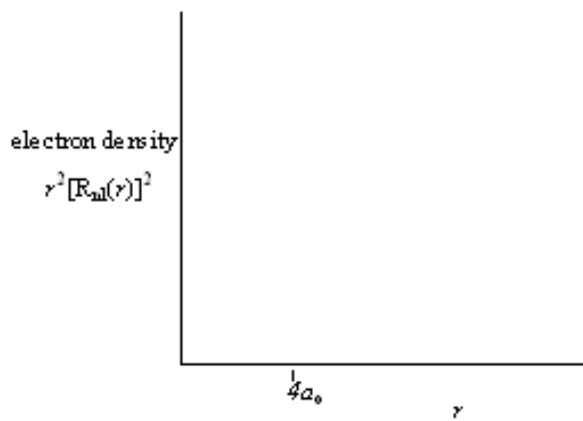
Lower limit : Z_{eff} = 2-1 = 1 when each 1s electron completely screen each other. In this case, IE = R = 1312 kJ/mol (or 13.604 eV) **R 이라고만 써도 1 점**

Upper limit : Z_{eff} = 2 if there is no screening at all. In this case, IE = 4R = 5248 kJ (or 54.417 eV) **4 R이라고만 써도 1 점**

[5] (10 points total) In the interpretation of atomic structure, Niels Bohr devised a model which has an analogy to the solar system. That is, in his model, electrons are circling around nucleus at a fixed distance, which is astonishingly successful in interpreting the observed atomic spectral lines. On the other hand, Max Born introduced a probability theory, with which the Schrödinger wave function becomes the quantum version of the Bohr electron orbits. Let's assume that one electron is located in hydrogen's 2s orbit (Bohr's model) or 2s orbital. **Draw below the electron density of 2s over distance** according to each case of Bohr's model and Born's theory.

(a) Bohr's Model

(b) Born's Theory

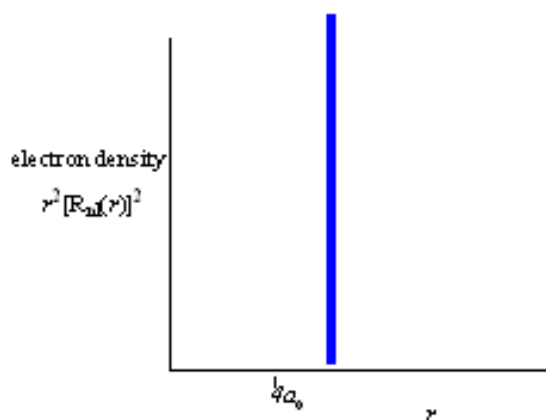


Answers)

(a) $4a_0$ 에서 close는 -1 점, far away:-2 점, correct explanation: 3 점

(b) r 값 틀리면 -2 점, graph 모양 틀리면 -2 점

(a) Bohr's Model



(b)



[6] (15 points total)

(i) (6 points) Wave functions have polynomial parts to them. The radial function $R_{nl}(r)$ is a polynomial in r of degree $n-1$ (highest power r^{n-1} , called a Laguerre polynomial) multiplied by an exponential function of the form $e^{-r/(na_0)}$, where a_0 is the Bohr radius. Similarly the angular function $Y_{lm}(\theta, \phi)$ consists of products of polynomials in $\sin(\theta)$ and $\cos(\theta)$ (called a Legendre function) multiplied by a complex exponential function $e^{im\phi}$ where $i = \sqrt{-1}$. As l increases from 0 to $n-1$, the number of nodes stays the same, but l of the radial nodes are exchanged for angular nodes, in the form of nodal planes or nodal cones. Algebraically, $R_{nl}(r)$ loses one root for an increase in l by one, and the degree of the $Y_{lm}(\theta, \phi)$ polynomial in $\sin(\theta)$ and $\cos(\theta)$ increases by one. Give the value of n , l and m for the following wave functions of the hydrogen-like atom ($\rho = Zr/a_0$):

$$(a) \Psi_a = \frac{1}{\sqrt{\pi}} \left(\frac{a_0}{Z} \right)^{-3/2} e^{-\rho}$$

$$(b) \Psi_b = \frac{1}{4\sqrt{2\pi}} \left(\frac{a_0}{Z} \right)^{-3/2} (2 - \rho) e^{-\rho/2}$$

$$(c) \Psi_c = \frac{1}{4\sqrt{2\pi}} \left(\frac{a_0}{Z} \right)^{-3/2} \rho e^{-\rho/2} \cos\theta$$

$$(d) \Psi_d = \frac{1}{81\sqrt{6\pi}} \left(\frac{a_0}{Z} \right)^{-3/2} \rho^2 e^{-\rho/3} (3\cos^2\theta - 1)$$

(ii) (4 points) Determine the number of radial nodes and angular nodes for each of the orbitals in (i) (that is for Ψ_a , Ψ_b , Ψ_c and Ψ_d).

(iii) (5 points) Complete the following table showing the properties of atomic orbitals. The first row is completed as an example.

Label	n	ℓ	No. of orbitals	No. of nodes	
				radial	angular
3d	3	2	5	0	2
2p		1		0	
	5	0			0
	4				3

(Answer)

(i) 각 0.5 점

(a) $n = 1, \ell = 0, m = 0$

(b) $n = 2, \ell = 0, m = 0$

(c) $n = 2, \ell = 1, m = 0$

(d) $n = 3, \ell = 2, m = 0$.

(ii) 각 0.5 점

(a) radial nodes = 0, angular nodes = 0

(b) radial nodes = 1, angular nodes = 0

(c) radial nodes = 0, angular nodes = 1

(d) radial nodes = 0, angular nodes = 2

(iii) 각 0.5 점

Label	n	ℓ	No. of orbitals	No. of nodes	
				radial	angular
3d	3	2	5	0	2
2p	2	1	3	0	1
5s	5	0	1	4	0
4f	4	3	7	0	3

[7] (10 points total) With regard to the nonmetal hydrides, consider the reactivity of ammonia (NH₃). Two ways of reactions of ammonia with water (only slightly though) can be postulated as follows (A or B):



(a) (2 points) Which reaction is more likely to occur ?

(b) (5 points) Write the plausible mechanism (electron movement) for your chosen reaction.

(c) (3 points) Describe the main reasons (at least two) for your answer (that is, why the chosen reaction occurs instead of the other).

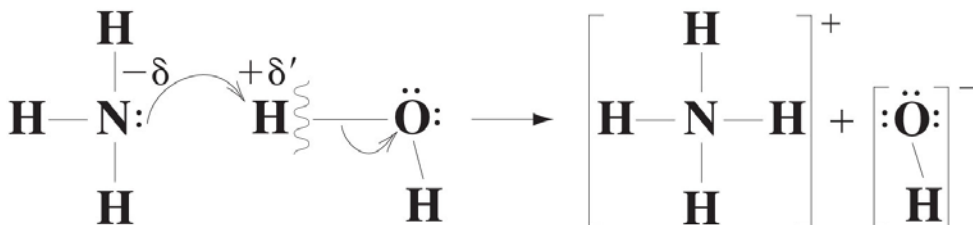
Answers)

(a) A 틀리면 0 점

(b) electron movement 틀리면 -2 점

product /reactant 틀리면 -2 점

charge 표시 안할 시 -1 점



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(c) i) N is less electronegative than O and more readily donates its electron pair

ii) the N-H bonds are less polar than O-H, making the ammonium hydrogen less susceptible to attack by nucleophiles

Bond의 polarity'와' 원자의 electronegativity 를 비교하여 정확히 언급 시 3 점

[8] (10 points total) Determine if the following statements are 'True' or 'False'.

A. (1 point) Fluorine is the most electronegative element, but its electron affinity is smaller than chlorine due to the small size of Fluorine's orbitals [ans. T](#)

B. (1 point) Ionization energy for fluorine is larger than that for chlorine because Z_{eff} for F is larger. [Ans. F \(n is smaller\)](#)

C. (1 point) $\text{Cs} < \text{Ba} < \text{Cd} < \text{Hg} < \text{P}$ is the right ordering for the ionization energies. [Ans. T](#)

D. (1 point) Atoms or ions with unpaired electrons are attracted into a magnetic field; they are paramagnetic. Then the Sc atom is paramagnetic, but the cation Sc^{1+} is not. [Ans. F 4s2d1 and 4s1d1](#)

E. (1 point) Transition metals of a given period have similar ionization energies because the first ionization is due to the ionization of ns valence electron. [Ans. T](#)

F. (1 point) Pauli exclusion principle is a consequence of quantum mechanics in which electrons cannot be distinguished from one another. [Ans. T](#)

G. (1 point) Unlike classical theory, the uncertainty principle implies that any particle interacting with another one will have nonzero kinetic energy, even at 0 K. [Ans. T](#)

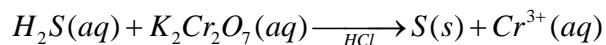
H. (1 point) Bohr's H atom model can be used to explain the origin of aufbau principle. [Ans. F](#)

I. (1 point) According to the aufbau principle, 5g orbitals will not be occupied even for the elements in 8th period. [Ans. F](#)

J. (1 point) Normalization constant for the wave function ensures that Pauli exclusion principle is observed for electron occupations. [Ans. F](#)

[9] (15 points total)

(a) (7 points) Balance the following redox reaction occurring in acidic aqueous solution by the half-reaction method. First write the equation in ionic form and eliminate spectator ions. When you have obtained a balanced ionic equation, add spectators to give a balanced neutral equation.

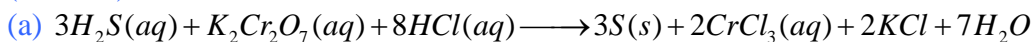


(b) (3 points) Identify which atom is reduced and the change of the oxidation number.

(c) (5 points) Place the following compounds in order of increasing acid strength and give reasons for your answer.

PO(OH)₃, SO₂(OH)₂, ClO₃(OH), ClO₂(OH), ClO(OH), Cl(OH)

(Answer)



화학식이 7 개이므로 각각 1 점, 그리고 구경꾼 이온 안 쓰면 -1 점

(b) Cr atom(1 점) is reduced from +6 to +3 (2 점).

(c) Cl(OH) < PO(OH)₃ < ClO(OH) < SO₂(OH)₂ < ClO₂(OH) < ClO₃(OH)

Acid strength increases with the increasing number of nonhydroxyl oxygens bonded to the central atom and the increasing electronegativity of the central nonmetal atom.

Order (3 점) Cl>S>P 경향 1 점, O4>O3>O2>O 경향 1 점

Explanation (2 점),

중심원소 전기음성도 1 점, 주변 산소 개수 증가 1 점

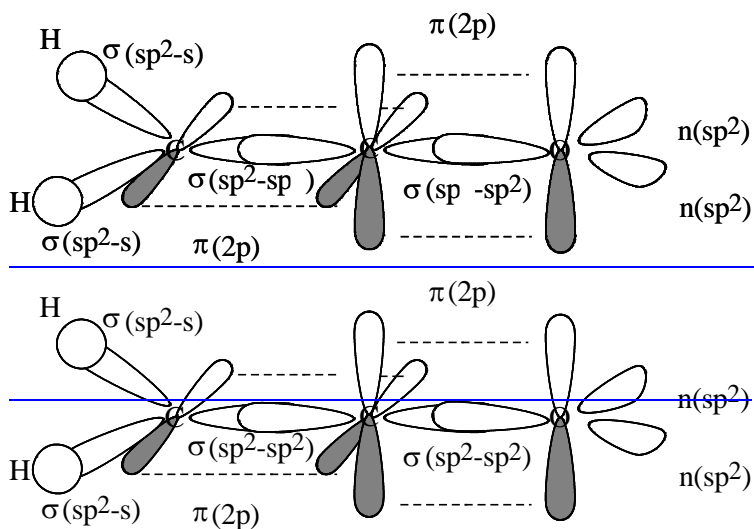
[1] (10 points total)

Use valence bond (VB) theory to predict the hybridization of the two carbon atoms in ketene (CH_2CO). Sketch the ~~overlap of hybrid~~ atomic orbitals depicting their ~~overlap~~ showing the σ - and π -bonding.

서식 있음: 강조 없음

Answers)

The central C of $\text{CH}_2=\text{C}=\text{O}$ ~~must form~~ a one π - π -bond on either each side. These π -bonds must be in are orthogonal planes and ~~must~~ involve the overlap of orthogonal 2p orbitals: the central C atom must be sp hybridized. The terminal C is sp^2 hybridized, as is the O atom.



(The atomic orbitals in the above diagram are elongated, for clarity)

2 points for the correct answer for the hybridization of the terminal (first) carbon (sp^2).
 2 points for the correct answer for the hybridization of the central (second) carbon (sp).
 1 point for each correct overlap (there are six overlaps)

[2] (15 points total)

Please consider the molecule of the formula ClF_3 .

(a) (6 points) Draw three possible structures of ClF_3 .

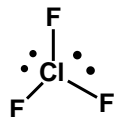
(b) (9 points) Select the most stable structure and give reasons for your answer.

Answers)

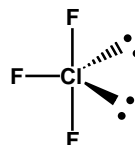
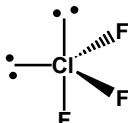
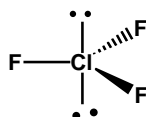
(a) 2 points for each correct structure

(b) 5 points for the correct structure, 4 points for correct reasons

5 electron pairs-domains around the central atom Cl



There are three possible structures.



90° lone pair-lone pair repulsion: 0

1

0

90° lone pair-bonding pair repulsion: 6

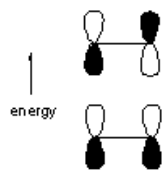
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\therefore The most stable structure is the T-shaped (the last one) geometry (the last one) due to the smallest number of 90° lone pair-long pair repulsion.

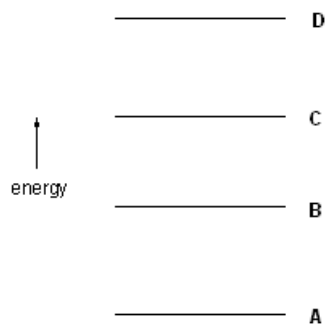
[3] (10 points total)

Interaction of two p orbitals on two adjacent centers yields a bonding and antibonding molecular orbital like below.



Now consider 1,3-butadiene ($\text{CH}_2\text{CHCHCH}_2$).

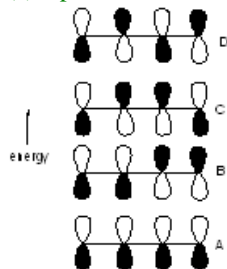
a) (4 points) By assuming that you have four p-orbitals on four adjacent carbon atoms, please construct the resulting four molecular orbitals below,



b) (6 points) Which orbital is the HOMO (highest occupied molecular orbital)?

Answers)

(a) 1 point for each correct answer (there are 4 MOs)



(b) HOMO: orbital B

[4] (15 points total)

Diatom molecule C_2 is a diatomic and diamagnetic molecule with a bond length (R_e) of 1.59 Å and a dissociation energy (D_e) of 6.3 eV.

a) (5 points) How many valence electrons are there for C_2 ? Assuming the perfect In accordance with the octet rule, draw the Lewis structure for C_2 and give-assign a bond order for this structure.

b) (4 points) What is are the MO electron configuration for C_2 ? and Provide the bond order for this e configuration.

c) (6 points) Write down MO electron configurations for the cation and anion of C_2 . What will be the order of R_e 's and D_e 's for C_2^+ , C_2 and C_2^- ?

Answers)

a) 8 valence electrons (1 point), $C \equiv C$ (2 points), bond order = 4 (2 points)

b) $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4$ (2 points), - bond order=2 (2 points)

c) cation $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^3$ bond order 1.5

anion $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2s})^1$ bond order 2.5

dissociation energy anion > neutral > cation (3 points)

bond length anion < neutral < cation (3 points)

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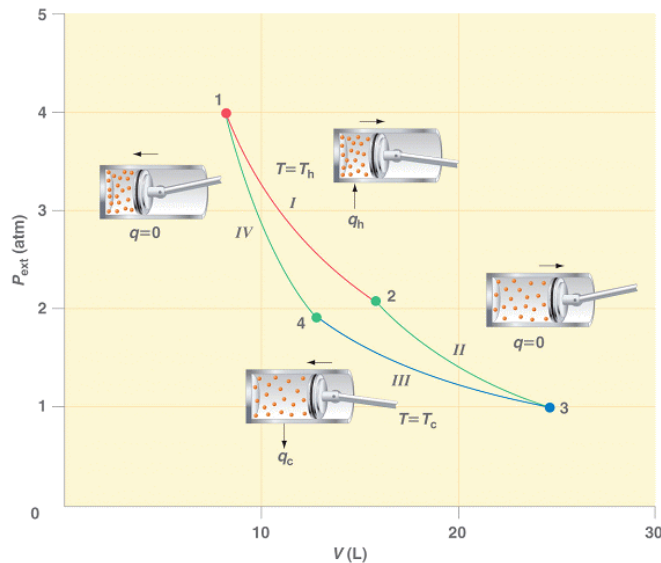
[5] (15 points total)

(a) (5 points) Assuming that 1 mol of ideal monoatomic gas is involved in the P-V diagram for the Carnot cycle, estimate the efficiency of the engine. We know the following numerical values exactly, $P_1=4$ atm, $V_1=8.21$ L, $P_3=1$ atm, $V_3=24.6$ L.

(b) (5 points) One can prove that PV^γ is constant ($\gamma = \frac{C_p}{C_v} = \frac{5}{3}$) for an adiabatic process.

By using this relationship, prove that $V_2=15.9$ L.

(c) (5 points) What is ΔS of the system going from state 1 to state 3? Express your answer in SI units.



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Answers)

(a)

$$T_h = (4.0 \text{ atm})(8.21 \text{ L}) / (0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1})(1 \text{ mol}) = 400 \text{ K}$$

$$T_c = (1.0 \text{ atm})(24.6 \text{ L}) / (0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1})(1 \text{ mol}) = 300 \text{ K}$$

$$\text{Efficiency } \varepsilon = (400-300)/400 = 0.25$$

(b) $P_1V_1 = P_2V_2$ for the isothermal process (from state 1 to state 2).

$$P_2V_2^\gamma = P_3V_3^\gamma \text{ for the adiabatic process (from state 2 to state 3)}$$

By combining the two equations, we have

$$V_2 = \left(\frac{P_3}{P_1V_1} V_3^\gamma \right)^{\frac{1}{\gamma-1}} = \left(\frac{1 \text{ atm}}{4 \text{ atm} \times 8.21 \text{ L}} (24.6 \text{ L})^{5/3} \right)^{\frac{1}{5/3-1}} = 15.9 \text{ L}$$

(c) For ΔS of the system going from state 1 to state 2,

$$\begin{aligned}
\Delta S_1 &= \int \frac{dq_{rev}}{T} = \frac{1}{T} \int dq_{rev} = \frac{q_{rev}}{T} = \frac{-w_{rev}}{T} = \frac{1}{T} \int_{V_1}^{V_2} P_{ext} dV \\
&= \frac{1}{T} \int_{V_1}^{V_2} P dV = \frac{1}{T} \int_{V_1}^{V_2} \frac{nRT}{V} dV = \frac{1}{T} nRT \ln \frac{V_2}{V_1} \\
&= nR \ln \frac{V_2}{V_1} = (1 \text{ mol}) \times (8.31447 \text{ JK}^{-1} \text{ mol}^{-1}) \times \ln\left(\frac{15.9}{8.21}\right) \\
&= 5.5 \text{ JK}^{-1}
\end{aligned}$$

For ΔS of the system going from state 2 to state 1,

$$\Delta S_2 = \int \frac{dq_{rev}}{T} = 0, \text{ because } q = 0.$$

So ΔS of the system going from state 1 to state 3,

$$\Delta S = \Delta S_1 + \Delta S_2 = 5.5 \text{ JK}^{-1}$$

[6] (10 points total)

A well-known intermediate molecule in the combustion and cracking of hydrocarbons is the methyl radical $\bullet\text{CH}_3$, where the dot indicates an unpaired electron.

(a) (5 points) Use data from Table 10.3 to estimate the heat of formation of $\bullet\text{CH}_3$.

(b) (5 points) Calculate the heat released in its combustion.

TABLE 10.3

Atomization and bond energies in kilocalories per mole

	$\Delta H_{\text{atomiz}}^\circ$	-H	-C	=C	≡C	-N	=N	≡N	-O	=O	-S	-Cl
H	52.1	104	99			93			110		81	103
C	171.3	99	83	147	194	70	147	213	84	174 ^a	62	78
N	113.0	93	70	147	213	38	100	226	48	150 ^b		48
O	59.2	110	84	174 ^a	256	48	150 ^b		33	118		49
S	66.6	81	62	114							55	60
P	75.2	76	63			50			84		55	79
F	18.9	135	105			65			44		68	44
Cl	29.1	103	78			48			49		60	58
Br	26.7	87	66			58					51	52
I	25.5	71	57						48			50

^aFor the double bonds in CO_2 , a better value to use is 192 kcal/mol (see text).

^bThis is the bond energy of NO , which has a bond order of 2½.

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(Answers)

This problem is almost identical to Example 10.7.

(a) The formation reaction is $\text{C}(s) + \frac{3}{2}\text{H}_2(g) \rightarrow \bullet\text{CH}_3(g)$ (2 points)

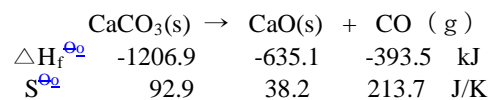
$$\Delta H_f^\circ = 171.3 + \left(\frac{3}{2}\right)104 - 3(99) = 30 \text{ kcal/mol (3 points)}$$

(b) The balanced combustion reaction is $4\text{CH}_3(g) + 7\text{O}_2(g) \rightarrow 4\text{CO}_2(g) + 6\text{H}_2\text{O}(g)$ (3 points)

$$\Delta H_{\text{comb}}^\circ = \frac{1}{4}[12(99) + 7(118) - 8(192) - 12(110)] = -210 \text{ kcal/mol (2 points)}$$

[7] (15 points total)

- (a) (5 points) What is ΔG^{\ominus} at 1000°C for the following reaction?
Please assume that ΔH^{\ominus} and ΔS^{\ominus} do not change with temperature.



- (b) (5 points) Is this reaction spontaneous at 1000°C and 1 atm ?
(c) (5 points) Find the temperature at which this reaction changes from being nonspontaneous to spontaneous.

Answers)

$$\begin{aligned} \text{(a)} \quad \Delta H^{\ominus} &= [(-635.1 - 393.5) - (-1206.9)]\text{kJ} = 178.3\text{kJ} \\ \Delta S^{\ominus} &= [(38.2 + 213.7) - (92.9)]\text{J/K} = 159.0\text{ J/K} \\ \Delta G^{\ominus} &= \Delta H^{\ominus} - T\Delta S^{\ominus} \\ &= 178.3\text{kJ} - (1273\text{K})(0.1590\text{kJ/K}) = -24.1\text{kJ} \end{aligned}$$

- (b) Since ΔG^{\ominus} is negative, the reaction should be spontaneous at 1000°C and 1 atm

$$\text{(c)} \quad \Delta G^{\ominus} = 0 = \Delta H^{\ominus} - T\Delta S^{\ominus}$$

$$T = \frac{\Delta H^{\ominus}}{\Delta S^{\ominus}} = \frac{178.3\text{kJ}}{0.159\text{kJ/K}} = 1121\text{K} (848^{\circ}\text{C})$$

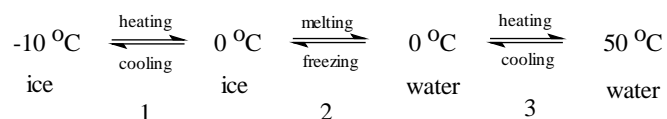
[8] (10 points total)

Exactly 1 mol of ice is heated reversibly at atmospheric pressure from $-10\text{ }^{\circ}\text{C}$ to $0\text{ }^{\circ}\text{C}$ and is then heated reversibly at atmospheric pressure from $0\text{ }^{\circ}\text{C}$ to $50\text{ }^{\circ}\text{C}$. Calculate ΔS for the system, surroundings and universe for this process.

[ΔH (fusion) of ice = 6.007 kJ mol^{-1} , specific heat capacity (c_p) of ice = $38.0\text{ J K}^{-1}\text{ mol}^{-1}$, specific heat capacity of water (c_p) = $75.0\text{ J K}^{-1}\text{ mol}^{-1}$. $0\text{ }^{\circ}\text{C} \equiv 273\text{ K}$.]

Answers)

For 1 mol of ice (at $-10\text{ }^{\circ}\text{C}$) \rightleftharpoons water (at $50\text{ }^{\circ}\text{C}$), the general scheme is



$$\Delta S_1 = n c_p \ln \left(\frac{T_2}{T_1} \right)$$

$$= 1 \times 38.0 \times \ln \left(\frac{273}{263} \right)$$

$$= 1.42\text{ J K}^{-1}\text{ mol}^{-1}$$

2 points

$$\Delta S_2 = \frac{\Delta H_{\text{fusion}}}{T_{\text{fusion}}}$$

$$= \frac{6007}{273}$$

$$= 22.0\text{ J K}^{-1}\text{ mol}^{-1}$$

2 points

$$\Delta S_3 = n c_p \ln \left(\frac{T_2}{T_1} \right)$$

$$= 1 \times 75.0 \times \ln \left(\frac{323}{273} \right)$$

$$= 12.6\text{ J K}^{-1}\text{ mol}^{-1}$$

2 points

$$\Delta S(\text{system}) = \Delta S_1 + \Delta S_2 + \Delta S_3$$

$$= 36.0\text{ J K}^{-1}\text{ mol}^{-1}$$

1 point

Because the whole process is reversible, $\Delta S(\text{surroundings})$ must be $-36.0\text{ J K}^{-1}\text{ mol}^{-1}$.

$$\text{Hence, } \Delta S(\text{universe}) = \Delta S(\text{system}) + \Delta S(\text{surroundings}) = 0$$

3 points