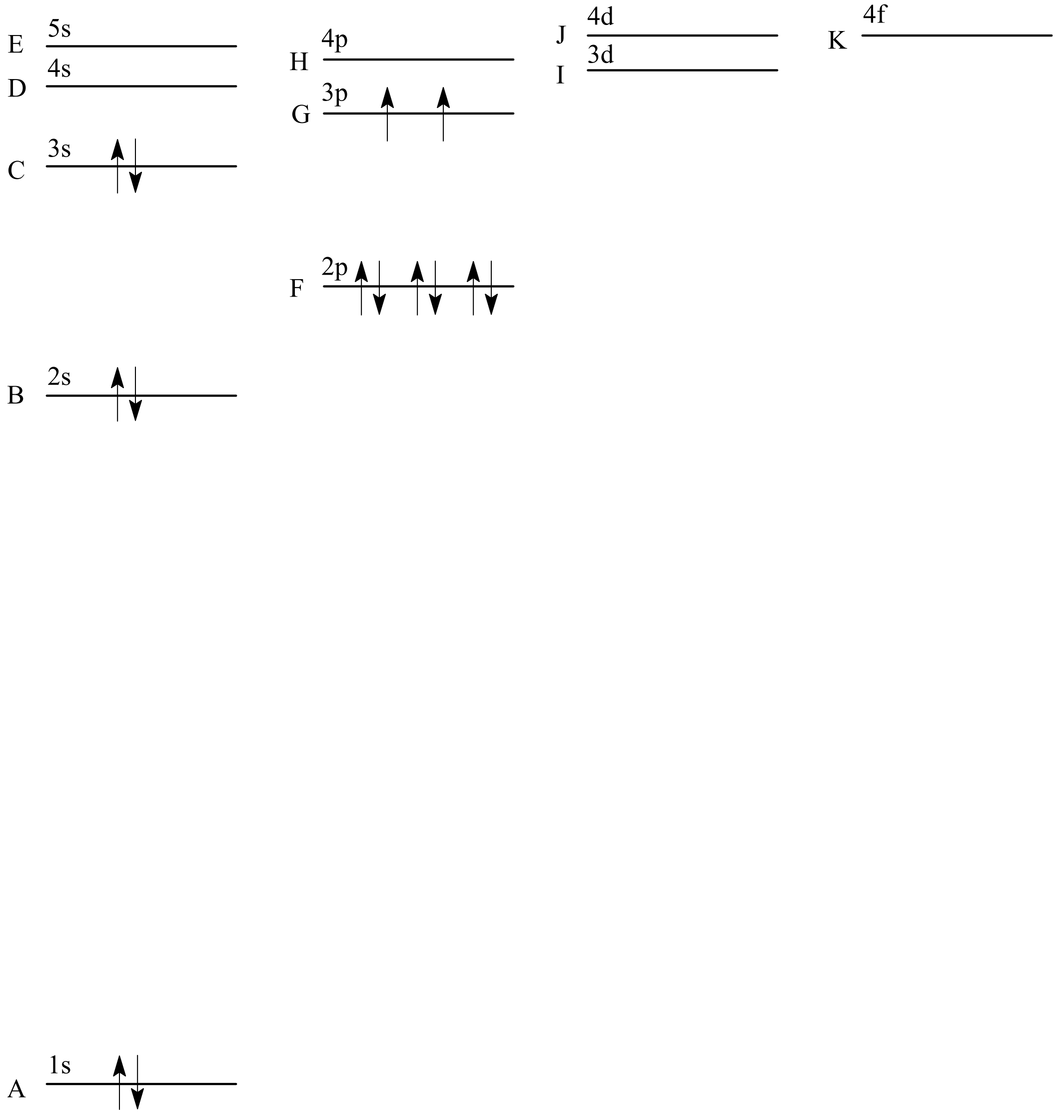
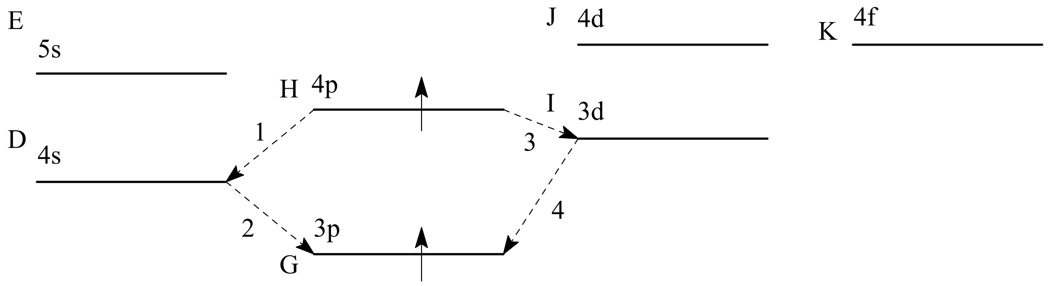
ChemE 2200 - Physical Chemistry II for Engineers
Solution to the First Preliminary Examination - 2025

1.(A) Si has 14 electrons. The orbital configuration is $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^2$. The Grotrian diagram, with orbital labels and electrons, is shown below.



(B) For the lowest energy state, Hund's rules dictate that the two 2p electrons are in different orbitals - for example $2p_x$ and $2p_y$. Also, the orbital state function for electrons 13 and 14 should be antisymmetric, such as $(2p_x)_{13}(2p_y)_{14} - (2p_y)_{13}(2p_x)_{14}$. Therefore the spin state function must be symmetric. For two spins there are three symmetric state functions: $\alpha_{13}\alpha_{14}$, $\beta_{13}\beta_{14}$, and $\alpha_{13}\beta_{14}+\beta_{13}\alpha_{14}$. Because there are three spin functions, the ground state is a triplet.

(C) The 4p electron will relax to the 3p level. The selection rules for the transitions are $\Delta\ell = \pm1$, Δn = anything. Thus there are two paths: 4p → 4s → 3p and 4p → 3d → 3p, as shown by the pertinent portion of the Grotrian diagram below.



The photon energies of the 4 transitions are:

1. $E_H - E_D$
2. $E_D - E_G$
3. $E_H - E_I$
4. $E_I - E_G$

Grading Rubric:

(A) 10 points total

Properly labeled atomic orbitals	4 points
Noted Si has 14 electrons	1 points
Properly allocated electrons to atomic orbitals	4 points
Observed Hund's Rules: the 2 electrons in 3p are unpaired.	1 point

(B) 2 points.

(C) Applied two criteria:

(1) $\Delta l = \pm 1$ for photon emission from electron transitions in multi-electron atoms.

(2) final level must have a vacancy to accept an electron.

2 points per proper photon energy.

Correct transitions but energies for photon *absorption*, not photon *emission* ($E_D - E_H$, etc) −2 points

2.(A) Principles applied:

- If two state functions overlap (are not orthogonal), linear combinations of the two state functions will yield state functions with higher and lower energy than either original state function.
- Molecular orbitals are named by considering their shape when viewed along the bond axis. Molecular orbitals with circular projections are named σ, molecular orbitals with two lobes are named π, and molecular orbitals with four lobes are named δ.

To determine if two atomic orbitals overlap, visualize two orbitals aligned along their *z* axis. The results for overlapping d orbitals are the same for overlapping p orbitals. That is, a p_z orbital on atom A overlaps with a p_z orbital on atom B. A p_z orbital on atom A has zero net overlap with a p_x orbital on atom B and zero net overlap with a p_y orbital on atom B.

A $3d_{z^2}$ orbital on atom A will overlap with another $3d_{z^2}$ orbital on atom B. We want the + lobes along the z axis to overlap, so the bonding molecular orbital is $(3d_{z^2})_A + (3d_{z^2})_B = (3d_{z^2})\sigma$. The antibonding orbital is $(3d_{z^2})_A - (3d_{z^2})_B = (3d_{z^2})\sigma^*$.

A $3d_{x^2-y^2}$ orbital on atom A will overlap with another $3d_{x^2-y^2}$ orbital on atom B. Imagine a $3d_{x^2-y^2}$ orbital directly above another $3d_{x^2-y^2}$ orbital. The unshaded lobes overlap and the shaded lobes overlap. Thus a sum of the $3d_{x^2-y^2}$ orbitals is a bonding molecular orbital. The molecular orbital looks like a d atomic orbital when viewed along the bond axis, so the molecular orbital is $(3d_{x^2-y^2})_A + (3d_{x^2-y^2})_B = (3d_{x^2-y^2})\delta$. The antibonding orbital is $(3d_{x^2-y^2})_A - (3d_{x^2-y^2})_B = (3d_{x^2-y^2})\delta^*$.

Similarly, the $3d_{xy}$ orbitals can be combined to form a bonding orbital: $(3d_{xy})_A + (3d_{xy})_B = (3d_{xy})\delta$. The antibonding orbital is $(3d_{xy})_A - (3d_{xy})_B = (3d_{xy})\delta^*$.

When a $3d_{xz}$ orbital is placed directly above another $3d_{xz}$ orbital, shaded lobes overlap unshaded lobes. So we need to change the sign on one of the atomic orbitals to form a bonding orbital. When viewed along the bond axis, the molecular orbital looks like a p atomic orbital, so it is designated a π molecular orbital: $(3d_{xz})_A - (3d_{xz})_B = (3d_{xz})\pi$. The antibonding orbital is $(3d_{xz})_A + (3d_{xz})_B = (3d_{xz})\pi^*$.

Similarly, the $3d_{yz}$ orbitals can be combined to form a bonding orbital: $(3d_{yz})_A - (3d_{yz})_B = (3d_{yz})\pi$. The antibonding orbital is $(3d_{yz})_A + (3d_{yz})_B = (3d_{yz})\pi^*$.

Summary:

bonding molecular orbitals	antibonding molecular orbitals
$3d_{z^2A} + 3d_{z^2B} = 3d_{z^2}\sigma$	$3d_{z^2A} - 3d_{z^2B} = 3d_{z^2}\sigma^*$
$3d_{x^2-y^2A} + 3d_{x^2-y^2B} = 3d_{x^2-y^2}\delta$	$3d_{x^2-y^2A} - 3d_{x^2-y^2B} = 3d_{x^2-y^2}\delta$
$3d_{xyA} + 3d_{xyB} = 3d_{xy}\delta$	$3d_{xyA} - 3d_{xyB} = 3d_{xy}\delta^*$
$3d_{xzA} - 3d_{xzB} = 3d_{xz}\pi$	$3d_{xzA} + 3d_{xzB} = 3d_{xz}\pi^*$
$3d_{yzA} - 3d_{yzB} = 3d_{yz}\pi$	$3d_{yzA} + 3d_{yzB} = 3d_{yz}\pi^*$

(B) Principle applied:

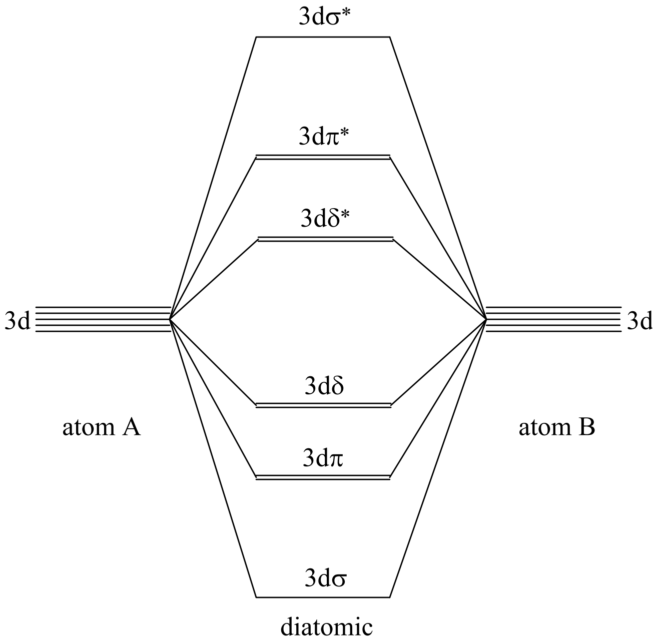
- The energy splitting is proportional to the overlap between the original state functions, the atomic orbitals.

We need to determine which atomic orbitals will overlap the most, for a given interatomic distance, *R*. The $3d_{z^2}$ orbitals project out along the bonding axis, so we expect these will overlap the most, like the $3p_z$ orbitals. Thus, we expect the $(3d_{z^2})\sigma$ to have the lowest energy and $(3d_{z^2})\sigma^*$ to have the highest energy.

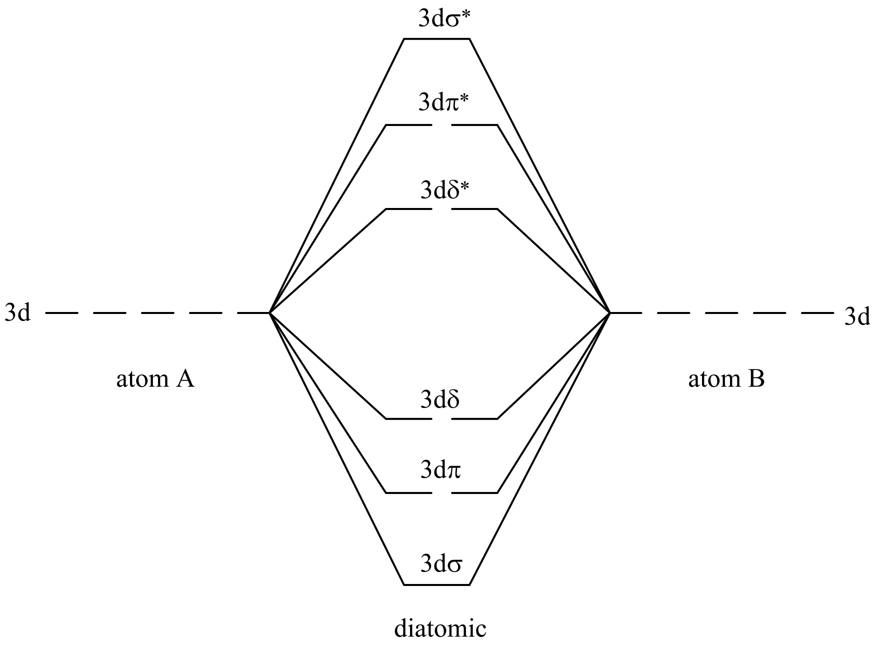
The $3d_{xz}$ and $3d_{yz}$ orbitals also project toward the other atom, not as much as the $3d_{z^2}$ orbitals but more than the $3d_{x^2-y^2}$ and $3d_{xy}$ orbitals. So we expect the π molecular orbitals to have the next highest energy splitting.

Finally, the δ molecular orbitals have the least overlap, so they will have the least energy splitting.

We expect the molecular-orbital energy-level diagram to look qualitatively as shown below.



The 3d atomic orbital levels are shown as five lines to indicate there are five orbitals. This is not to imply there is any energy difference between the levels; all five 3d atomic energy levels are the same. The same for the π and δ molecular orbitals. Or the molecular-orbital energy-level diagram can be depicted as shown below.



Grading Rubric:

(A) 21 points total.

Molecular Orbitals: 15 points

3 points for each bonding and anti-bonding pair.

−1 point for wrong sign between atomic orbitals

−1 point for wrong molecular orbital label: σ, π, or δ.

Which atomic orbitals to combine? 3 points. Must mention ‘overlap’ or ‘non-orthogonal.’

Naming principle: 3 points. Must mention symmetry when viewed along bond axis: spherical = σ, two lobes = π and 4 lobes = δ.

(B) Molecular-Orbital Energy-Level diagram: 9 points total

Diagram has atomic energy levels (3d) on left and right sides and molecular orbitals in the middle. Diagonal lines from the atomic orbitals to the molecular orbitals. Levels are symmetrically spaced above and below atomic orbitals 3 points

σ and σ* are the lowest and highest energies, respectively, equally spaced higher and lower. 2 points

π and π* are the next lowest and next highest energies, respectively, equally spaced higher and lower. 2 points

δ and δ* are the middle energies, respectively, equally spaced higher and lower. 2 points

3. The key feature in these pure rotational spectra is the spacing between the peaks, $2B$. The rotational constant B depends on the rotational moment of inertia, I.

$$B = \frac{\hbar}{4\pi c I}$$

The rotational moment of inertia depends on the reduced mass and the bond length, R.

$$I = \mu R^2 = \frac{m_A m_B}{m_A + m_B} R^2$$

The bond lengths for $^{10}B^{14}N$ and $^{11}B^{15}N$ are the same. The difference is the reduced mass.

$$I_{^{11}B^{15}N} = \frac{(11)(15)}{11+15} R^2 = 6.35R^2$$

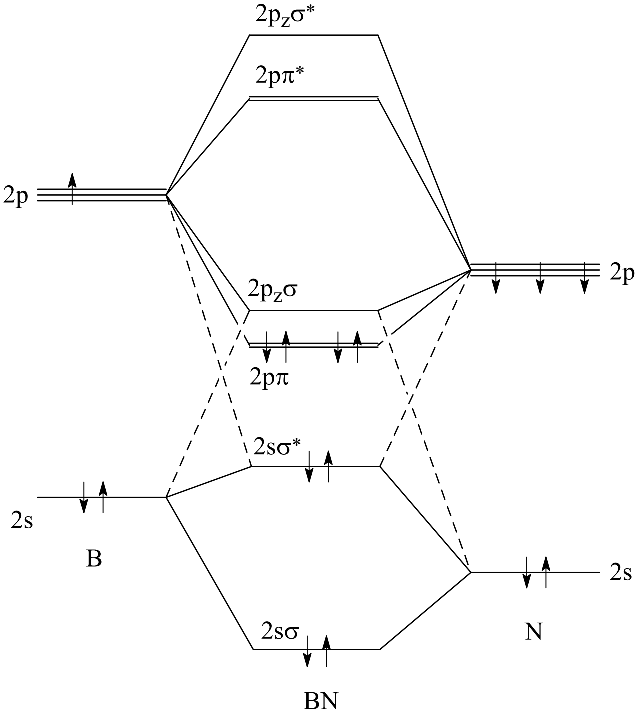
$$I_{^{10}B^{14}N} = \frac{(10)(14)}{10+14} R^2 = 5.83R^2$$

The ratio of the rotational constants is inversely proportional to the ratio of rotational moments of inertia.

$$\frac{B_{^{11}\mathrm{B}^{15}\mathrm{N}}}{B_{^{10}\mathrm{B}^{14}\mathrm{N}}} = \frac{I_{^{10}\mathrm{B}^{14}\mathrm{N}}}{I_{^{11}\mathrm{B}^{15}\mathrm{N}}} = \frac{5.83R^2}{6.35R^2} = 0.92$$

The peak spacing in the $^{11}\mathrm{B}^{15}\mathrm{N}$ spectrum is smaller than the peak spacing in the $^{10}\mathrm{B}^{14}\mathrm{N}$ spectrum.

Compare the rotational constants of $^{11}\mathrm{B}^{15}\mathrm{N}$ and $^{11}\mathrm{B}^{15}\mathrm{N}^+$. These have the same mass (within 0.002%). We must examine the bond length, *R*, to predict the effect on the rotational moment of inertia. Sketch a molecular orbital energy level diagram for BN.



The bond order for $^{11}\mathrm{B}^{15}\mathrm{N}$ is ½(6–2) = 2. The missing electron in $^{11}\mathrm{B}^{15}\mathrm{N}^+$ comes from the 2pπ bonding orbital and the bond order decreases to ½(5–2) = 1½. Thus the bond length of $^{11}\mathrm{B}^{15}\mathrm{N}^+$ is longer than the bond length of $^{11}\mathrm{B}^{15}\mathrm{N}$.

$$I_{^{11}\mathrm{B}^{15}\mathrm{N}} < I_{^{11}\mathrm{B}^{15}\mathrm{N}^+}$$
$$B_{^{11}\mathrm{B}^{15}\mathrm{N}} > B_{^{11}\mathrm{B}^{15}\mathrm{N}^+}$$

The peak spacing in the $^{11}\mathrm{B}^{15}\mathrm{N}$ spectrum is larger than the peak spacing in the $^{11}\mathrm{B}^{15}\mathrm{N}^+$ spectrum.

So the $^{10}\mathrm{B}^{14}\mathrm{N}$ spectrum has the largest peak spacing, the $^{11}\mathrm{B}^{15}\mathrm{N}$ spectrum has the intermediate peak spacing, and the $^{11}\mathrm{B}^{15}\mathrm{N}^+$ spectrum has the smallest peak spacing.

Thus spectrum A is $^{11}\mathrm{B}^{15}\mathrm{N}^+$, spectrum B is $^{10}\mathrm{B}^{14}\mathrm{N}$ and spectrum C is $^{11}\mathrm{B}^{15}\mathrm{N}$.

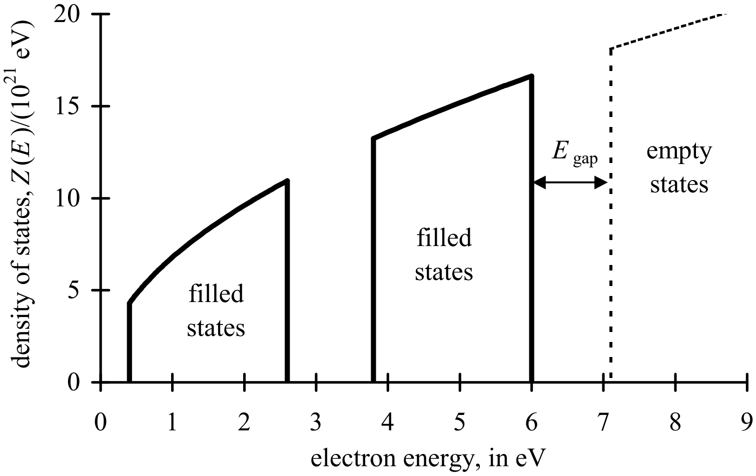
Grading Rubric:

Noted key spectral feature is *B* and analyzed spectra: Spectrum A has smallest *B*, Spectrum B has the largest *B*. 4 points

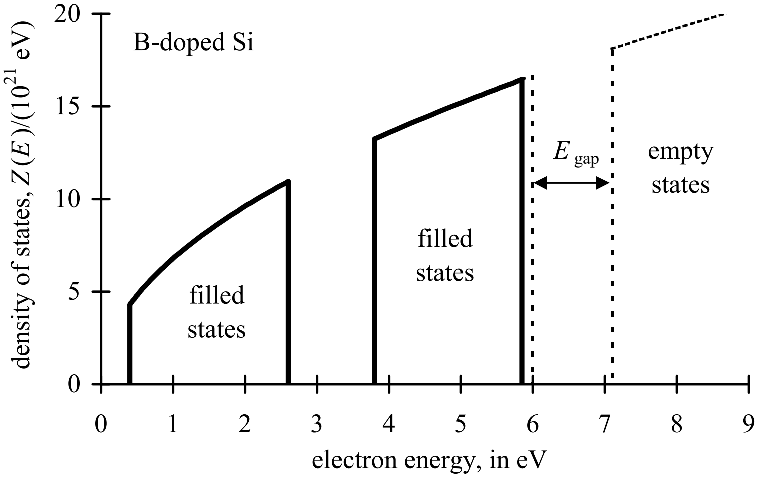
$^{10}\mathrm{B}^{14}\mathrm{N}$ vs $^{11}\mathrm{B}^{15}\mathrm{N}$	9 points total
Noted same bond length, but different masses	2 points
Calculated μ and *I* for both	3 points
Calculated ratio of *I*s and related to ratio of *B*s.	2 points
B($^{10}\mathrm{B}^{14}\mathrm{N}$) > B($^{11}\mathrm{B}^{15}\mathrm{N}$)	2 points
$^{11}\mathrm{B}^{15}\mathrm{N}$ vs $^{11}\mathrm{B}^{15}\mathrm{N}^+$	9 points total

Noted same masses but different bond lengths	2 points
Drew molecular-orbital energy-level diagram	3 points
Bond order of $^{11}B^{15}N = 2$ and bond order of $^{11}B^{15}N^{+} = 1½$	2 points
$I(^{11}B^{15}N) < I(^{11}B^{15}N^{+})$ and $B(^{11}B^{15}N) > I(^{11}B^{15}N^{+})$	2 points
Overall Ranking: $B(^{10}B^{14}N) > B(^{11}B^{15}N) > I(^{11}B^{15}N^{+})$	1 point
Assignments: Spectrum A = $^{11}B^{15}N^{+}$, Spectrum B = $^{10}B^{14}N$ and Spectrum C = $^{11}B^{15}N$.	2 points

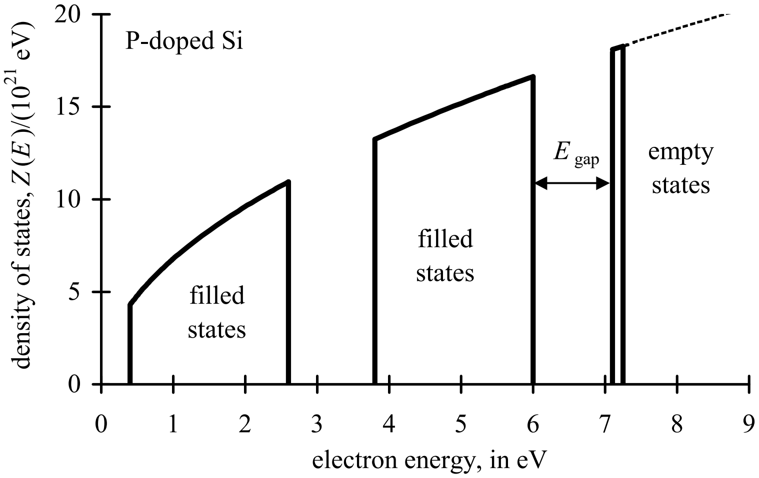
4. Silicon has four valence electrons. Thus the first two bands are filled and the states above the band gap are empty. The occupancy of states for silicon are shown in the figure below.



Boron has three valance electrons. Every silicon atom replaced by a boron atom creates a vacancy in the valence band below the band gap. Boron-doped silicon is a metallic conductor, as shown in the figure below.



Phosphorus has five valance electrons. Phosphorus-doped silicon has electrons in the conduction band and thus is also a metallic conductor, as shown in the figure below.



Electrons flow through the P-doped Si by traveling in the conduction band. These electrons have energies above the band gap. When one of these electrons flows into the B-doped Si, the electron still has energy above the band gap. But B-doped Si has vacancies in the valence band. The electron falls to a state below the band gap. Thus the photon energy is 7.1 – 6.0 = 1.1 eV.

Grading Rubric:

Energy of emitted photon 5 points. (2 points for lower band gap, 3.8 – 2.6 = 1.2 eV)

Explanation: Si has 4 valence electrons; two bands filled. 2 points

P-doped Si has electrons in the conduction band. 2 points

B-doped Si has vacancies in the conduction band. 2 points

P-doped Si and B-doped Si are metallic conductors. 2 points

Electron from P-doped Si enters B-doped Si at 7.1 eV. Electron in B-doped Si falls to vacant state in the valence band at 6.0 eV. Energy difference (7.1 – 6.0 eV = 1.1 eV) is energy of emitted photon. 7 points

5. Begin by calculating the temperatures for states 1 and 2.

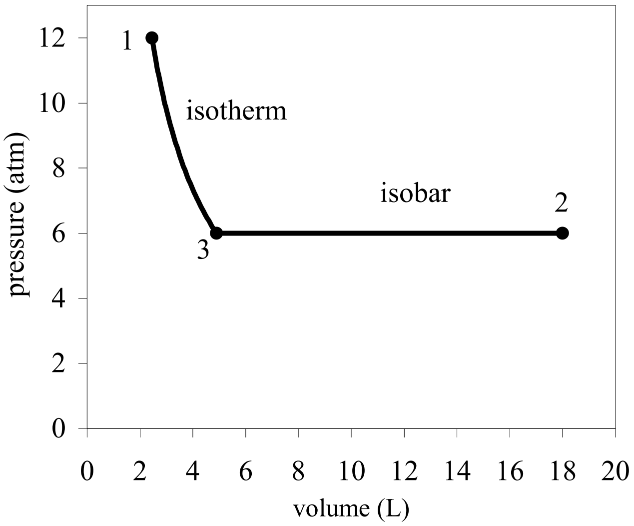
$$T_1 = \frac{P_1V_1}{nR} = \frac{(12\text{ atm})(2.45\text{ L})}{(1\text{ mol})(0.0821\text{ L}\cdot\text{atm/(mol}\cdot\text{K)}} = 358\text{ K}$$

$$T_2 = \frac{P_2V_2}{nR} = \frac{(6.0\text{ atm})(18\text{ L})}{(1\text{ mol})(0.0821\text{ L}\cdot\text{atm/(mol}\cdot\text{K)}} = 1315\text{ K}$$

(A) Start at State 1 and devise the isothermal path at 358 K to lower pressure. The isothermal path will intersect the isobaric path at P_3 = 6.0 atm. Calculate the volume at the intersection (state 3).

$$V_3 = \frac{nRT_3}{P_3} = \frac{(1\text{ mol})(0.0821\text{ L}\cdot\text{atm/(mol}\cdot\text{K)}(358\text{ K})}{6.0\text{ atm}} = 4.90\text{ L}$$

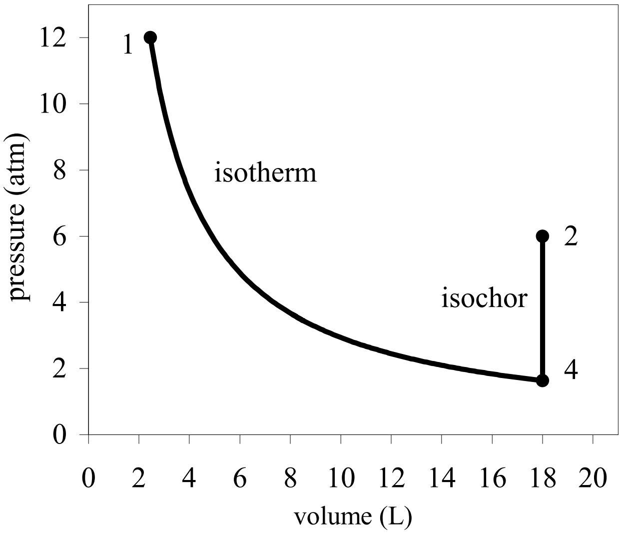
The isothermal expansion starts at state 1 (12.0 atm, 2.45 L, and 358 K) and goes downward on a *P*-*V* map to state 3 (6.00 atm, 4.90 L, and 358 K). The isobaric compression starts at state 3 (6.00 atm, 4.90 L, and 358 K) and expands to state 2 (6.00 atm, 18.0 L, and 1315 K). These paths are plotted below. (A plot was not necessary.)



(B) Start at state 1 and devise the isothermal path at 358 K to lower pressure. The isothermal path will intersect the isochoric path at $V = 18$ L. Calculate the pressure at the intersection (state 4).

$$P_4 = \frac{nRT_4}{V_4} = \frac{(1\text{ mol})(0.0821\text{ L}\cdot\text{atm/(mol}\cdot\text{K)}(358\text{ K})}{18\text{ L}} = 1.63\text{ atm}$$

Because P_4 is lower than P_2, we need isochoric compression from state 4 to state 2.
The isothermal expansion starts at state 1 (12.0 atm, 2.45 L, and 358 K) and goes downward and to the right on a P-V map to state 4 (1.63 atm, 18.0 L, and 358 K). The isochoric compression starts at state 4 (1.63 atm, 18.0 L, and 358 K) and compresses to state 2 (6.00 atm, 18.0 L, and 1315 K). These paths are plotted below. (A plot was not necessary.)



(C) Use the isothermal to isochoric paths to calculate ΔU because ΔU for the isothermal path is zero and calculating ΔU for the isochoric path is straightforward. Because O_2 is a diatomic ideal gas, $\overline{C}_V = (5/2)R$.

$$\Delta U_{1\to2} = \Delta U_{1\to4} + \Delta U_{4\to2} = 0 + n\int_{T_4}^{T_2}\overline{C}_V dT = n\frac{5}{2}R(T_2 - T_4)$$

$$= (1.0\text{ mol})\frac{5}{2}(8.314\text{ J/(K}\cdot\text{mol))}(1315\text{ K} - 358\text{ K}) = +19.89\text{ kJ}$$

On a P-V map, state 2 is above the isothermal path that passes through state 1. (Recall $\Delta U = 0$ for any state on the isothermal path through state 1.) Therefore we expect $\Delta U_{1\to2} > 0$, which is consistent with the result.

(D) Use the isothermal to isobaric paths to calculate ΔH because ΔH for the isothermal path is zero and calculating ΔH for the isobaric path is straightforward. Because O_2 is a diatomic ideal gas, $\overline{C}_P = \overline{C}_V + R = (7/2)R$.

$$\Delta H_{1\to 2} = \Delta H_{1\to 3} + \Delta H_{3\to 2} = 0 + n\int_{T_3}^{T_2} \overline{C}_P dT = -n\frac{7}{2}R(T_3 - T_2)$$

$$= (1.0\text{ mol})\frac{7}{2}(8.314\text{ J}/(\text{K}\cdot\text{mol}))(1315\text{ K} - 358\text{ K}) = +27.85\text{ kJ}$$

On a P-V map, state 2 is above the isothermal path that passes through state 1. (Recall $\Delta H = 0$ for any state on the isothermal path through state 1.) Therefore we expect $\Delta H_{1\to 2} > 0$, which is consistent with the result.

An alternative method is to use ΔU to calculate ΔH from the definition of ΔH.

$$\begin{aligned}
H &= U + PV \\
\Delta H_{1\to 2} &= \Delta U_{1\to 2} + \Delta(PV)_{1\to 2} \\
&= \Delta U_{1\to 2} + P_2V_2 - P_1V_1 \\
&= +19.89\text{ kJ} + ((6.0\text{ atm})(18\text{ L}) - (12.0\text{ atm})(2.45\text{ L}))(0.101\text{ kJ/L}\cdot\text{atm}) \\
&= +19.89\text{ kJ} + 7.94\text{ kJ} = +27.83\text{ kJ}
\end{aligned}$$

A common error was to expand $\Delta(PV)$ to $(\Delta P)(\Delta V)$.

Grading Rubric:

(A) 5 points total. $T_3 = 358$ K (2 points), $V_3 = 4.90$ L (2 points), $P_3 = 6.00$ atm (1 point)

(B) 6 points total. $T_4 = 358$ K (2 points), $V_4 = 18.00$ L (2 points), $P_4 = 1.63$ atm (2 points)

(C) 7 points total.

Expression for ΔU	3 points
Value for C_V (2 points)	
Numerical answer	2 points

(D) 7 points total.

Expression for ΔH	3 points
Value for C_P (2 points)	
Numerical answer	2 points