

Question 1:

(a) How does Zeroth law of thermodynamics lead to concept of temperature?

- The Zeroth Law of Thermodynamics states that if two thermodynamic systems are each in thermal equilibrium with a third system, then they are in thermal equilibrium with each other.
- This law implies the existence of a property, called temperature, that determines whether two systems are in thermal equilibrium.
- When two systems are in thermal equilibrium, their temperatures are equal.
- The Zeroth Law allows for the construction of thermometers and the definition of a temperature scale, as it provides a basis for comparing the thermal states of different bodies.

(b) How does the first-order differ from the second-order phase transitions?

- **First-order phase transitions** are characterized by a discontinuous change in the first derivatives of the Gibbs free energy with respect to temperature and pressure (e.g., entropy, volume).
 - Examples include melting, boiling, and sublimation.
 - They involve a latent heat, meaning that heat is absorbed or released without a change in temperature during the transition.
 - There is a discontinuity in properties like density, specific heat, and thermal expansivity at the transition point.
- **Second-order phase transitions** are characterized by a continuous change in the first derivatives of the Gibbs free energy, but a discontinuous change in the second derivatives (e.g., specific heat, thermal expansivity, compressibility).
 - Examples include the ferromagnetic-paramagnetic transition (Curie point) and the transition to superconductivity.
 - They do not involve a latent heat.

- There is no discontinuity in entropy or volume at the transition point.

(c) Show that $(\partial U / \partial V)_T = 0$ for an ideal gas.

- For a general thermodynamic system, the internal energy U can be expressed as a function of temperature T and volume V , i.e., $U = U(T, V)$.
- The differential of internal energy is given by $dU = (\partial U / \partial T)_V dT + (\partial U / \partial V)_T dV$.
- We also know from the first law of thermodynamics that $dU = \delta Q - \delta W = TdS - PdV$.
- For an ideal gas, the internal energy is solely a function of temperature, meaning $U = U(T)$. This is a fundamental property derived from experimental observations (Joule's experiment).
- If U depends only on T , then the change in U with respect to V at constant T must be zero.
- Therefore, $(\partial U / \partial V)_T = 0$ for an ideal gas.

(d) Explain the need for the second law of thermodynamics when the energy conservation law exists.

- The **First Law of Thermodynamics (Energy Conservation Law)** states that energy cannot be created or destroyed, only transformed from one form to another. It tells us that energy is conserved in any process.
- However, the First Law does not provide any information about the *direction* of a spontaneous process or the *quality* of energy. For example, it allows for heat to flow from a colder body to a hotter body, which is never observed spontaneously. It also allows for the complete conversion of heat into work, which is not possible in a cyclic process.
- The **Second Law of Thermodynamics** addresses these limitations by introducing the concept of entropy. It states that the total entropy of an isolated system can only increase over time, or remain constant in ideal cases (reversible processes).

- It defines the direction of spontaneous processes (e.g., heat flows from hot to cold, processes move towards a state of greater disorder).
- It sets limits on the efficiency of heat engines and refrigerators, stating that 100% efficiency in converting heat to work in a cyclic process is impossible.
- In essence, the First Law tells us what is *possible* in terms of energy transformations, while the Second Law tells us what is *probable* and in which direction natural processes will occur.

(e) Can the change in entropy be a negative quantity? Support your answer.

- Yes, the change in entropy can be a negative quantity for a *specific part* of a system or a *non-isolated system*.
- For example, when a gas is compressed isothermally, its entropy decreases because its disorder decreases.
- When water freezes into ice, the entropy of the water decreases because it transitions from a more disordered liquid state to a more ordered solid state.
- However, the Second Law of Thermodynamics states that for an **isolated system**, the total entropy must either increase ($\Delta S \geq 0$) for irreversible processes or remain constant ($\Delta S = 0$) for reversible processes.
- If the entropy of one part of a system decreases, there must be a corresponding, and even larger, increase in entropy elsewhere in the system or its surroundings, ensuring that the total entropy of the universe or the isolated system always increases or stays the same.

(f) Calculate the root mean square speed of oxygen molecules at 300K. Take mass of oxygen molecule as 5.31×10^{-26} kg.

- The root mean square (RMS) speed v_{rms} of gas molecules is given by the formula: $v_{rms} = \sqrt{(3kT)/m}$ Where:
 - k is the Boltzmann constant (1.38×10^{-23} J/K)
 - T is the absolute temperature (300 K)

- m is the mass of one molecule (5.31×10^{-26} kg)
- Substitute the given values into the formula: $v_{rms} = \sqrt{(3 \times 1.38 \times 10^{-23} \text{ J/K} \times 300 \text{ K}) / (5.31 \times 10^{-26} \text{ kg})}$ $v_{rms} = \sqrt{(1242 \times 10^{-23}) / (5.31 \times 10^{-26})}$ $v_{rms} = \sqrt{233.898 \times 10^3}$ $v_{rms} = \sqrt{233898}$ $v_{rms} \approx 483.63 \text{ m/s}$

(g) Discuss the limitations of Van der Waal's equation of state.

- Van der Waals' equation of state is: $(P + a(n/V)^2)(V - nb) = nRT$.
- **Approximation for Intermolecular Forces:** The term $a(n/V)^2$ accounts for attractive forces between molecules. However, it is an average correction and does not accurately represent the complex, short-range nature of these forces. It oversimplifies the attractive interactions, especially at high densities.
- **Approximation for Molecular Volume:** The term $(V - nb)$ accounts for the finite volume occupied by the gas molecules. This 'b' (excluded volume) is assumed to be constant, whereas in reality, the effective volume occupied by molecules can change with temperature and pressure due to molecular vibrations and overlapping. It treats molecules as rigid spheres, which is not always accurate.
- **Inaccuracies at High Densities and Low Temperatures:** While an improvement over the ideal gas law, Van der Waals' equation still shows significant deviations from experimental results at very high pressures and very low temperatures, where intermolecular forces become dominant and the assumptions made in its derivation break down.
- **No Prediction of Phase Transitions Accurately:** Although it qualitatively predicts the liquid-gas phase transition and the critical point, it doesn't accurately describe the coexistence region of liquid and gas. It often predicts oscillations in the P-V isotherms in the two-phase region, which are not physically observed. Maxwell's equal area rule is needed to correct this.

- **Ignores Molecular Shape and Quantum Effects:** The equation assumes spherical molecules and does not account for the shape of molecules or quantum mechanical effects that become important at very low temperatures or high densities.

Question 2:

(a) What is Adiabatic Lapse Rate? Derive an expression for the rate of change of temperature with height during the adiabatic gas expansion. How does the presence of water vapour in air affect this process? (6 marks)

- **Adiabatic Lapse Rate:** The adiabatic lapse rate is the rate at which the temperature of an air parcel changes as it rises or falls in the atmosphere, assuming no heat exchange with the surrounding environment (adiabatic process). As an air parcel rises, the surrounding atmospheric pressure decreases, causing the parcel to expand and cool. Conversely, as it sinks, it is compressed and warms.
- **Derivation of an expression for the rate of change of temperature with height during adiabatic gas expansion:**
 - Consider a parcel of ideal gas undergoing an adiabatic process. From the first law of thermodynamics, for an adiabatic process, $dQ = 0$, so $dU = -dW$.
 - For a gas, $dU = nC_V dT$ and $dW = PdV$.
 - Thus, $nC_V dT = -PdV$. (Equation 1)
 - For an ideal gas, $PV = nRT$, so $P = nRT/V$.
 - Substitute P into Equation 1: $nC_V dT = -(nRT/V)dV$.
 - $C_V dT = -(RT/V)dV$.
 - Rearrange: $dT/T = -(R/C_V)(dV/V)$.
 - We know that $C_P - C_V = R$, so $R/C_V = (C_P - C_V)/C_V = \gamma - 1$.
 - Therefore, $dT/T = -(\gamma - 1)(dV/V)$.

- Now, consider the change in pressure with height. If a gas parcel rises by a small height dh , the change in pressure dP is related to the density ρ and acceleration due to gravity g by $dP = -\rho g dh$. (Negative sign indicates pressure decreases with height).
- For an ideal gas, $\rho = nM/V$, where M is molar mass. So $V = nM/\rho$.
- Also, from $PV = nRT$, $V/n = RT/P$.
- From $P = \rho RT/M$, we have $\rho = PM/(RT)$.
- Substitute ρ into the pressure equation: $dP = -(PM/(RT))g dh$.
- $dP/P = -(Mg/RT)dh$.
- We have $T^{\gamma-1}P^{-\gamma} = \text{constant}$ for an adiabatic process. Taking logarithm and differentiating: $(\gamma - 1)d(\ln T) - \gamma d(\ln P) = 0$ $(\gamma - 1)(dT/T) - \gamma(dP/P) = 0$ $dT/T = (\gamma/(\gamma - 1))(dP/P)$.
- Substitute dP/P : $dT/T = (\gamma/(\gamma - 1))(-(Mg/RT)dh)$.
- $dT = -(\gamma/(\gamma - 1))(Mg/R)dh$.
- The adiabatic lapse rate is dT/dh : $dT/dh = -(\gamma/(\gamma - 1))(Mg/R)$.
- Since $R = N_A k_B$ and $M = mN_A$, where N_A is Avogadro's number, k_B is Boltzmann constant, and m is mass of one molecule. Alternatively, use molar gas constant R .
- We can also write it in terms of specific heat capacities: $R/M = C_p - C_v$ per unit mass.
- $dT/dh = -g/((C_p - C_v)/(\gamma - 1)) = -g/((C_p - C_v)/((C_p/C_v) - 1)) = -g/(C_v)$. This isn't quite right.
- Using $C_p - C_v = R$ and $\gamma = C_p/C_v$: $dT/dh = -(\gamma - 1)g/R_s$, where R_s is specific gas constant (R/M). Or, the widely used form for dry adiabatic lapse rate (DALR) is $\Gamma_d = g/C_p$. To derive this from $nC_v dT = -PdV$: $dU = -dW$. $d(nC_v T) = -PdV$. Also, $P = \rho gh$. This derivation is slightly involved. Let's restart from $dT/T =$

$(\gamma/(\gamma - 1))(dP/P)$. From hydrostatic equation, $dP = -\rho g dh$. For ideal gas, $\rho = PM/(RT)$, where M is molar mass. $dP = -(PMg/(RT))dh$. So, $dP/P = -(Mg/(RT))dh$. Substitute this into the adiabatic relation: $dT/T = (\gamma/(\gamma - 1))(-(Mg/(RT))dh)$. $dT = -(\gamma/(\gamma - 1))(Mg/R)(T/T)dh$. $dT/dh = -(\gamma/(\gamma - 1))(Mg/R)$. Using $R = C_p - C_v$ and $C_p/C_v = \gamma$, so $C_v = R/(\gamma - 1)$ and $C_p = \gamma R/(\gamma - 1)$. Mg/R is related to g/R_s . The standard dry adiabatic lapse rate $\Gamma_d = g/C_p$ (where C_p is specific heat capacity at constant pressure per unit mass). Let's use the fundamental relation for an adiabatic process for a parcel of gas: $dQ = C_p dT - V dP = 0$ (This is incorrect. $TdS = dU + PdV$ and $dS = 0$ for adiabatic.) For an adiabatic process, $PV^\gamma = \text{constant}$. Also, for an ideal gas, $PV = RT$. We consider an air parcel moving vertically in the atmosphere. Assume the parcel is always in pressure equilibrium with its surroundings. The hydrostatic equation is $dP = -\rho g dh$. For an adiabatic process, $TdS = dU + PdV = 0$. Also, $dU = C_v dT$ and $PdV = d(PV) - VdP = d(RT) - VdP = RdT - VdP$. So $C_v dT + RdT - VdP = 0 \Rightarrow C_p dT - VdP = 0$. $C_p dT = VdP$. Substitute $V = RT/P$: $C_p dT = (RT/P)dP$. $dT = (R/C_p)(T/P)dP$. Now substitute $dP = -\rho g dh = -(PM/RT)g dh$: $dT = (R/C_p)(T/P)(-(PM/RT)g dh)$. $dT = -(R/C_p)(M/R)g dh$. $dT = -(M/C_p)g dh$. The adiabatic lapse rate is $dT/dh = -Mg/C_p$. This is the dry adiabatic lapse rate for a dry ideal gas. Here C_p is molar specific heat capacity at constant pressure. If C_p is specific heat capacity per unit mass, then we directly have $dT/dh = -g/C_p$.

- **How does the presence of water vapour in air affect this process?**
 - The presence of water vapor significantly affects the adiabatic lapse rate by introducing **latent heat** effects.
 - When a moist air parcel rises and cools to its dew point, water vapor begins to condense into liquid water or ice.
 - This condensation process releases latent heat into the air parcel.

- The release of latent heat partially offsets the cooling due to expansion, causing the temperature to decrease at a slower rate than the dry adiabatic lapse rate.
- This slower rate is called the **moist adiabatic lapse rate** (or saturated adiabatic lapse rate), which is typically around $4 - 7 \text{ }^\circ\text{C/km}$, significantly less than the dry adiabatic lapse rate of approximately $9.8 \text{ }^\circ\text{C/km}$.
- The amount of latent heat released depends on the amount of water vapor condensing, making the moist adiabatic lapse rate variable.

(b) One mole of an ideal gas ($\gamma = 1.4$) initially kept at 27°C is adiabatically compressed so that its pressure becomes 10 times its original value. Calculate its temperature after compression and work done on the gas. (6 marks)

• Given:

- $n = 1 \text{ mole}$
- $\gamma = 1.4$
- $T_1 = 27^\circ\text{C} = 27 + 273.15 = 300.15 \text{ K}$
- $P_2 = 10P_1$

• **Temperature after compression (T_2):**

- For an adiabatic process, the relationship between pressure and temperature is $P^{(1-\gamma)}T^\gamma = \text{constant}$ or $P_1^{(1-\gamma)}T_1^\gamma = P_2^{(1-\gamma)}T_2^\gamma$.
- $T_2^\gamma/T_1^\gamma = P_1^{(\gamma-1)}/P_2^{(\gamma-1)}$
- $(T_2/T_1)^\gamma = (P_1/P_2)^{(\gamma-1)}$
- $T_2/T_1 = (P_1/P_2)^{(\gamma-1)/\gamma}$
- $T_2 = T_1(P_1/P_2)^{(\gamma-1)/\gamma}$
- $P_1/P_2 = 1/10 = 0.1$

- $(\gamma - 1)/\gamma = (1.4 - 1)/1.4 = 0.4/1.4 = 2/7 \approx 0.2857$
- $T_2 = 300.15 \text{ K} \times (0.1)^{2/7}$
- $T_2 = 300.15 \text{ K} \times (0.1)^{0.2857}$
- $T_2 \approx 300.15 \text{ K} \times 0.5369$
- $T_2 \approx 555.24 \text{ K}$ or $555.24 - 273.15 = 282.09 \text{ }^\circ\text{C}$.

• **Work done on the gas (W):**

- For an adiabatic process, the work done on the gas is given by $W = nC_V(T_2 - T_1)$.
- We need to find C_V . For an ideal gas, $C_P - C_V = R$, and $\gamma = C_P/C_V$.
- So, $\gamma C_V - C_V = R \Rightarrow C_V(\gamma - 1) = R \Rightarrow C_V = R/(\gamma - 1)$.
- $C_V = 8.31 \text{ J/mole-K}/(1.4 - 1) = 8.31 \text{ J/mole-K}/0.4 = 20.775 \text{ J/mole-K}$.
- $W = 1 \text{ mole} \times 20.775 \text{ J/mole-K} \times (555.24 \text{ K} - 300.15 \text{ K})$
- $W = 20.775 \text{ J/K} \times 255.09 \text{ K}$
- $W \approx 5299.7 \text{ J}$ or 5.30 kJ .

(c) Show that the 100% efficiency of a reversible Carnot's heat engine violates laws of thermodynamics. (6 marks)

• **Violates the Second Law of Thermodynamics:**

- The efficiency of a reversible Carnot engine is given by $\eta = 1 - T_C/T_H$, where T_C is the temperature of the cold reservoir and T_H is the temperature of the hot reservoir.
- For the efficiency to be 100% ($\eta = 1$), it would require $T_C/T_H = 0$, which implies $T_C = 0 \text{ K}$ (absolute zero).

- Achieving absolute zero is impossible according to the **Third Law of Thermodynamics**, which states that it is impossible to reach absolute zero in a finite number of steps.
- Even if T_C were achievable, 100% efficiency implies that all the heat absorbed from the hot reservoir is converted entirely into work, with no heat rejected to the cold reservoir ($Q_C = 0$).
- This directly contradicts the **Kelvin-Planck statement of the Second Law of Thermodynamics**, which states that it is impossible to construct a device operating in a cycle whose sole effect is the absorption of heat from a single thermal reservoir and the production of an equivalent amount of work. Such a machine is called a perpetual motion machine of the second kind.
- If a 100% efficient engine existed, it could be used to continuously extract heat from a single reservoir (e.g., the ocean or atmosphere) and convert it into useful work without any other effect, which would effectively create energy from nothing in the long run by depleting a reservoir's thermal energy without a cold sink, fundamentally violating the Second Law.
- **Indirectly related to the First Law (but primarily Second Law):**
 - While primarily a violation of the Second Law, a 100% efficient engine also implies that entropy of the universe would decrease or remain constant during a process that converts heat to work without heat rejection, which contradicts the fundamental principle that natural processes increase the entropy of the universe.
 - If heat is converted entirely to work, it implies no increase in the disorder of the surroundings or the system. This is a very specific condition not allowed by the Second Law in practice.

Question 3:

(a) If two Carnot engines A and B are operated in series such that engine A absorbs heat at temperature T_1 and rejects heat to the sink at temperature T_2 , while engine

B absorbs half of the heat rejected by engine A and rejects heat to the sink at temperature T_3 . If the work done in both cases is equal, show that $T_1 - T_3 = 2T_2$. (6 marks)

• **Engine A:**

- Absorbs heat Q_1 at T_1 .
- Rejects heat Q_2 at T_2 .
- Work done $W_A = Q_1 - Q_2$.
- For a Carnot engine, $Q_1/T_1 = Q_2/T_2$. So $Q_2 = Q_1(T_2/T_1)$.
- $W_A = Q_1 - Q_1(T_2/T_1) = Q_1(1 - T_2/T_1) = Q_1(T_1 - T_2)/T_1$.

• **Engine B:**

- Absorbs heat Q'_1 at T_2 .
- Given that $Q'_1 = Q_2/2$.
- Rejects heat Q_3 at T_3 .
- Work done $W_B = Q'_1 - Q_3$.
- For a Carnot engine, $Q'_1/T_2 = Q_3/T_3$. So $Q_3 = Q'_1(T_3/T_2)$.
- $W_B = Q'_1 - Q'_1(T_3/T_2) = Q'_1(1 - T_3/T_2) = Q'_1(T_2 - T_3)/T_2$.
- Substitute $Q'_1 = Q_2/2$: $W_B = (Q_2/2)(T_2 - T_3)/T_2$.
- Substitute $Q_2 = Q_1(T_2/T_1)$: $W_B = (Q_1(T_2/T_1)/2)(T_2 - T_3)/T_2 = (Q_1/2T_1)(T_2 - T_3)$.

• **Given $W_A = W_B$:**

- $Q_1(T_1 - T_2)/T_1 = (Q_1/2T_1)(T_2 - T_3)$
- Cancel Q_1/T_1 from both sides:
- $(T_1 - T_2) = (1/2)(T_2 - T_3)$

- $2(T_1 - T_2) = T_2 - T_3$
- $2T_1 - 2T_2 = T_2 - T_3$
- $2T_1 - T_3 = 3T_2$
- Wait, the question asks to show $T_1 - T_3 = 2T_2$. Let me recheck the problem statement and my derivation.
- If $2T_1 - 2T_2 = T_2 - T_3$, then $2T_1 = 3T_2 - T_3$. This isn't $T_1 - T_3 = 2T_2$.
- Let's check the given relation: $T_1 - T_3 = 2T_2 \Rightarrow T_1 = 2T_2 + T_3$.
- Substituting this into my derived relation: $2(2T_2 + T_3) - 2T_2 = T_2 - T_3$.
- $4T_2 + 2T_3 - 2T_2 = T_2 - T_3$.
- $2T_2 + 2T_3 = T_2 - T_3$.
- $T_2 = -3T_3$. This is impossible as temperatures must be positive in Kelvin.
- There might be a mistake in the problem statement or my interpretation/calculation.
- Let's re-examine $W_B = (Q_2/2)(T_2 - T_3)/T_2$.
- $W_B = (Q_1(T_2/T_1)/2)(T_2 - T_3)/T_2 = (Q_1/2T_1)(T_2 - T_3)$. This step looks correct.
- $W_A = Q_1(T_1 - T_2)/T_1$. This also looks correct.
- $Q_1(T_1 - T_2)/T_1 = (Q_1/2T_1)(T_2 - T_3)$.
- $(T_1 - T_2) = (1/2)(T_2 - T_3)$.
- $2T_1 - 2T_2 = T_2 - T_3$.
- $2T_1 = 3T_2 - T_3$. This is the result from the given conditions.

- If the question implies T_1, T_2, T_3 are related in a specific arithmetic progression for the problem statement to be true, then the statement $T_1 - T_3 = 2T_2$ might be a target identity that needs re-evaluation of assumptions.
- Let's assume the question means "show that $2T_1 = 3T_2 - T_3$ ". Or perhaps there's a typo in the question's target result.
- If T_1, T_2, T_3 are temperatures of successive heat baths, and the engines are in series, then often the rejected heat from the first is the absorbed heat for the second, but here it's "half of the heat rejected".
- The derivation above $2T_1 = 3T_2 - T_3$ appears correct based on the problem statement.
- It is possible that the problem means $T_1 - T_2 = T_2 - T_3$ (equal temperature drops) which implies $T_1 + T_3 = 2T_2$ (arithmetic progression). But that's not what the problem states explicitly or implies from the work being equal for "half the heat absorbed".
- Let's re-read carefully: "absorbs half of the heat rejected by engine A". This is $Q'_1 = Q_2/2$. This is what I used.
- The derived relation is $2T_1 - 2T_2 = T_2 - T_3 \Rightarrow 2T_1 = 3T_2 - T_3$.
- The target relation is $T_1 - T_3 = 2T_2$. Let's assume there is a typo in the question and the target should be $2T_1 = 3T_2 - T_3$.

(b) The heat capacity of a given crystal of mass m at very low temperature varies like T^3 . Calculate the entropy of the crystal as a function of temperature. (6 marks)

- Given that the heat capacity $C(T)$ of the crystal at very low temperature varies like T^3 .
 - So, we can write $C(T) = aT^3$, where 'a' is a constant.
- The change in entropy dS is related to heat capacity by the definition $dS = dQ_{rev}/T$.

- For a constant volume process, $dQ_{rev} = C_V dT$. At very low temperatures, $C_P \approx C_V = C(T)$.
- So, $dS = (C(T)/T)dT = (aT^3/T)dT = aT^2 dT$.
- To find the entropy $S(T)$ as a function of temperature, we integrate dS from absolute zero (where entropy is zero according to the Third Law of Thermodynamics for a perfect crystal) to a temperature T .
- $S(T) - S(0) = \int_0^T a T'^2 dT'$.
- Since $S(0) = 0$ for a perfect crystal at $T = 0$:
 - $S(T) = \int_0^T a T'^2 dT'$
 - $S(T) = a[T'^3/3]_0^T$
 - $S(T) = (a/3)T^3$.
- Therefore, the entropy of the crystal as a function of temperature is proportional to T^3 .

(c) Show that transfer of heat from a body at higher temperature to a body at lower temperature or vice versa leads to increase of entropy of the interacting system. (6 marks)

- Consider two bodies, A and B, in thermal contact.
- Body A is at a higher temperature T_A and Body B is at a lower temperature T_B , where $T_A > T_B$.
- Let a small amount of heat δQ flow from body A to body B.
- **Change in entropy of Body A:**
 - Since Body A loses heat, its entropy change is $\Delta S_A = -\delta Q/T_A$. (The negative sign indicates loss of entropy).
- **Change in entropy of Body B:**

- Since Body B gains heat, its entropy change is $\Delta S_B = +\delta Q/T_B$. (The positive sign indicates gain of entropy).
- **Total change in entropy of the interacting system (Body A + Body B):**
 - $\Delta S_{total} = \Delta S_A + \Delta S_B = -\delta Q/T_A + \delta Q/T_B$
 - $\Delta S_{total} = \delta Q(1/T_B - 1/T_A)$
 - $\Delta S_{total} = \delta Q((T_A - T_B)/(T_A T_B))$.
- Since heat flows from higher temperature to lower temperature, $T_A > T_B$, which means $(T_A - T_B) > 0$.
- Also, temperatures T_A and T_B are absolute temperatures and are always positive (> 0). And δQ is positive.
- Therefore, $\Delta S_{total} > 0$. This shows that the transfer of heat from a higher temperature body to a lower temperature body leads to an **increase in the total entropy** of the interacting system, consistent with the Second Law of Thermodynamics for spontaneous processes.
- **What if heat flows from lower to higher temperature (vice versa as mentioned in question)?**
 - Such a process is not spontaneous. It requires external work (like in a refrigerator or heat pump).
 - If heat were to spontaneously flow from T_B to T_A (where $T_B < T_A$), then:
 - $\Delta S_A = +\delta Q/T_A$
 - $\Delta S_B = -\delta Q/T_B$
 - $\Delta S_{total} = \delta Q(1/T_A - 1/T_B) = \delta Q((T_B - T_A)/(T_A T_B))$.
 - Since $T_B < T_A$, $(T_B - T_A) < 0$.
 - Therefore, $\Delta S_{total} < 0$.

- This negative change in entropy for a spontaneous process violates the Second Law of Thermodynamics. This confirms why heat does not spontaneously flow from a colder body to a hotter body.

Question 4 (Using Maxwell's equation to prove (any two)):

(a) $C_P - C_V = T\alpha_V^2/\beta_T$ (c) $TdS = C_P dT - TV\alpha_P dP$

• **Maxwell's Relations:**

- $(\partial T / \partial V)_S = -(\partial P / \partial S)_V$
- $(\partial T / \partial P)_S = (\partial V / \partial S)_P$
- $(\partial S / \partial V)_T = (\partial P / \partial T)_V$
- $(\partial S / \partial P)_T = -(\partial V / \partial T)_P$

• **Definitions:**

- Specific heat at constant volume: $C_V = T(\partial S / \partial T)_V$
- Specific heat at constant pressure: $C_P = T(\partial S / \partial T)_P$
- Coefficient of volume expansion: $\alpha_P = (1/V)(\partial V / \partial T)_P$
- Isothermal compressibility: $\beta_T = -(1/V)(\partial V / \partial P)_T$

(a) Show that $C_P - C_V = T\alpha_V^2/\beta_T$

- We know that S can be considered a function of T and V , or T and P .
- If $S = S(T, V)$, then $dS = (\partial S / \partial T)_V dT + (\partial S / \partial V)_T dV$.
- If $S = S(T, P)$, then $dS = (\partial S / \partial T)_P dT + (\partial S / \partial P)_T dP$.
- From the second expression for dS , for a constant pressure process ($dP = 0$), $dS = (\partial S / \partial T)_P dT$.
 - So, $C_P = T(\partial S / \partial T)_P$.
- For a constant volume process ($dV = 0$) from the first expression for dS : $dS = (\partial S / \partial T)_V dT$.

- So, $C_V = T(\partial S / \partial T)_V$.
- We can also write dS in terms of T and V , and T and P .
 - Consider $S(T, P)$. The total differential of S is $dS = (\partial S / \partial T)_P dT + (\partial S / \partial P)_T dP$.
 - Consider $S(T, V)$. The total differential of S is $dS = (\partial S / \partial T)_V dT + (\partial S / \partial V)_T dV$.
 - Equating the dS expressions: $(\partial S / \partial T)_P dT + (\partial S / \partial P)_T dP = (\partial S / \partial T)_V dT + (\partial S / \partial V)_T dV$.
 - Divide by dT at constant P : $(\partial S / \partial T)_P = (\partial S / \partial T)_V + (\partial S / \partial V)_T (\partial V / \partial T)_P$.
 - Multiply by T : $T(\partial S / \partial T)_P = T(\partial S / \partial T)_V + T(\partial S / \partial V)_T (\partial V / \partial T)_P$.
 - Substitute C_P and C_V : $C_P = C_V + T(\partial S / \partial V)_T (\partial V / \partial T)_P$.
 - From Maxwell's fourth relation: $(\partial S / \partial V)_T = (\partial P / \partial T)_V$.
 - So, $C_P - C_V = T(\partial P / \partial T)_V (\partial V / \partial T)_P$.
 - We know the cyclic relation: $(\partial P / \partial T)_V (\partial T / \partial V)_P (\partial V / \partial P)_T = -1$.
 - Therefore, $(\partial P / \partial T)_V = -(\partial P / \partial V)_T (\partial V / \partial T)_P$.
 - Substitute this into the expression for $C_P - C_V$: $C_P - C_V = T[-(\partial P / \partial V)_T (\partial V / \partial T)_P] (\partial V / \partial T)_P$
 $C_P - C_V = -T(\partial P / \partial V)_T [(\partial V / \partial T)_P]^2$.
 - Now, recall the definitions of α_P and β_T : $\alpha_P = (1/V)(\partial V / \partial T)_P \Rightarrow (\partial V / \partial T)_P = V\alpha_P$. $\beta_T = -(1/V)(\partial V / \partial P)_T \Rightarrow (\partial P / \partial V)_T = -1/(V\beta_T)$.
 - Substitute these into the equation for $C_P - C_V$: $C_P - C_V = -T[-1/(V\beta_T)][V\alpha_P]^2$
 $C_P - C_V = T(1/(V\beta_T))(V^2\alpha_P^2)$
 $C_P - C_V = TV\alpha_P^2/\beta_T$.

- The question has $T\alpha_V^2/\beta_T$. The α_V likely refers to α_P , the coefficient of volume expansion at constant pressure, often just written as α . The result derived is $TV\alpha_P^2/\beta_T$. The V is missing in the question. Assuming it's a typo in the question and the formula is $C_P - C_V = TV\alpha_P^2/\beta_T$.

(c) Show that $TdS = C_P dT - TV\alpha_P dP$

- We start with the general expression for dS as a function of T and P : $dS = (\partial S / \partial T)_P dT + (\partial S / \partial P)_T dP$.
- From the definition of C_P : $C_P = T(\partial S / \partial T)_P \Rightarrow (\partial S / \partial T)_P = C_P / T$.
- From Maxwell's relation: $(\partial S / \partial P)_T = -(\partial V / \partial T)_P$.
- From the definition of coefficient of volume expansion α_P : $(\partial V / \partial T)_P = V\alpha_P$.
- Substitute these into the dS expression: $dS = (C_P / T) dT - V\alpha_P dP$.
- Multiply the entire equation by T : $TdS = C_P dT - TV\alpha_P dP$.
- This proves the relation.

Question 5:

(a) Show using Clausius-Clapeyron's latent heat equation that substances which expands on melting have their melting point raised by the increasing pressure, whereas those that contract on melting get their melting points lowered by the increase of pressure. (6 marks)

- **Clausius-Clapeyron Latent Heat Equation:**
 - $(dP/dT) = L/(T\Delta V)$, where:
 - dP/dT is the slope of the phase boundary curve in the P-T diagram (the change in pressure with respect to temperature along the melting curve).
 - L is the latent heat of melting (heat absorbed during melting).

- T is the melting temperature (absolute temperature).
- $\Delta V = V_{liquid} - V_{solid}$ is the change in volume during melting (volume of liquid minus volume of solid).
- **Case 1: Substance expands on melting.**
 - If a substance expands on melting, then $V_{liquid} > V_{solid}$, which means $\Delta V = V_{liquid} - V_{solid} > 0$.
 - The latent heat of melting L is always positive (heat is absorbed during melting).
 - The temperature T is absolute temperature, so $T > 0$.
 - Therefore, for substances that expand on melting, $dP/dT = L/(T\Delta V)$ will be positive (> 0).
 - A positive dP/dT means that as pressure P increases, the melting temperature T also increases. In other words, increasing pressure raises the melting point.
 - Examples: Most substances like iron, copper, gold, etc.
- **Case 2: Substance contracts on melting.**
 - If a substance contracts on melting, then $V_{liquid} < V_{solid}$, which means $\Delta V = V_{liquid} - V_{solid} < 0$.
 - The latent heat of melting L is positive, and T is positive.
 - Therefore, for substances that contract on melting, $dP/dT = L/(T\Delta V)$ will be negative (< 0) because ΔV is negative.
 - A negative dP/dT means that as pressure P increases, the melting temperature T decreases. In other words, increasing pressure lowers the melting point.

- Example: Water (ice melts to water, and water is denser than ice, so $V_{\text{water}} < V_{\text{ice}}$). This property is crucial for processes like ice skating (pressure from skates melts a thin layer of ice).

(b) Draw the pressure-volume isotherms obtained by Andrew's experiments on CO_2 . Discuss the deviations observed from expected ideal gas behavior. (6 marks)

- **Andrew's Experiments on CO_2 and P-V Isotherms:**

- (Cannot draw diagrams as per instructions)
- Andrew's experiments involved studying the P-V behavior of CO_2 at various constant temperatures (isotherms).
- **Isotherms above critical temperature ($T > T_c$):** At high temperatures (e.g., 48°C), the isotherms resemble those of an ideal gas. As pressure increases, volume decreases smoothly, following Boyle's law fairly well. There is no clear distinction between gas and liquid phases. The substance remains a gas at all pressures.
- **Isotherm at critical temperature ($T = T_c$):** At the critical temperature (31.1°C for CO_2), the isotherm exhibits a horizontal inflection point. This point is called the critical point. At this temperature, the substance exists as a critical fluid, where the liquid and gas phases are indistinguishable. There is no latent heat of vaporization at the critical point.
- **Isotherms below critical temperature ($T < T_c$):** At temperatures below the critical temperature (e.g., 13.1°C , 21.5°C), the isotherms show distinct regions:
 - i. **Gaseous region:** At low pressures, the substance behaves like an ideal gas. As pressure increases, the volume decreases.
 - ii. **Liquefaction region (horizontal plateau):** At a certain pressure (saturation vapor pressure), the gas starts to condense into a liquid. During this phase transition, the volume decreases significantly at constant pressure as more and more gas turns into liquid. This region appears as a horizontal straight line on

the P-V diagram. This plateau represents the coexistence of liquid and vapor phases.

iii. **Liquid region:** Once all the gas has condensed into liquid, a very large increase in pressure is required to produce a small decrease in volume. This indicates that the liquid phase is almost incompressible, and the isotherm becomes very steep.

- **Deviations observed from expected ideal gas behavior:**

- **Phase Transitions:** Ideal gases are assumed to remain in the gaseous state regardless of pressure or temperature. Andrew's experiments clearly show the existence of liquid and gaseous phases and the transition between them, which is not accounted for by the ideal gas law.
- **Liquefaction:** The ideal gas law does not predict liquefaction. The horizontal plateaus in Andrew's isotherms, representing the constant pressure condensation of gas to liquid, are a significant deviation from ideal gas behavior.
- **Finite Molecular Size and Intermolecular Forces:** The ideal gas law assumes point-like molecules with no intermolecular forces. Andrew's results highlight that real gases have finite molecular sizes and experience attractive intermolecular forces, especially at high pressures and low temperatures. These forces cause the gas to condense.
- **Critical Point:** The concept of a critical temperature and critical pressure, where the distinction between liquid and gas vanishes, is completely absent from the ideal gas model.
- **Incompressibility of Liquid:** The steepness of the isotherms in the liquid phase demonstrates the high incompressibility of liquids, which is a significant deviation from the infinitely compressible nature implied by the ideal gas law at high pressures.

(c) How can Van der Waals's equation of state explain Andrew's experiment results? (6 marks)

- Van der Waals' equation of state is: $(P + a(n/V)^2)(V - nb) = nRT$.
 - The 'b' term $(V - nb)$ accounts for the finite volume occupied by the gas molecules. This means the actual volume available for molecular motion is less than the total volume of the container. This explains why at very high pressures, the volume does not drop to zero but approaches 'nb', showing the finite size of molecules.
 - The 'a' term $(a(n/V)^2)$ accounts for the attractive intermolecular forces. These forces tend to pull molecules closer together, effectively reducing the pressure exerted by the gas on the container walls. This explains the deviation from ideal gas behavior at lower temperatures and higher pressures, where these forces become more significant and lead to condensation.
- **Qualitative Explanation of Andrew's Isotherms:**
 - **High Temperatures ($T > T_c$):** At high temperatures, the kinetic energy of molecules is large, so the attractive forces (represented by 'a') have a smaller effect, and the molecular volume (represented by 'b') is also less dominant. In this region, the Van der Waals equation reduces to something closer to the ideal gas law, qualitatively matching the observed smooth isotherms.
 - **Critical Temperature ($T = T_c$):** The Van der Waals equation, when plotted for specific isotherms, can show an inflection point at the critical temperature, corresponding to the critical point observed by Andrews. At this point, $(\partial P / \partial V)_T = 0$ and $(\partial^2 P / \partial V^2)_T = 0$. Solving these for the Van der Waals equation gives the critical constants in terms of 'a' and 'b', thus providing a theoretical basis for the critical phenomenon.
 - **Low Temperatures ($T < T_c$):** Below the critical temperature, the Van der Waals equation predicts S-shaped isotherms with a maximum and a minimum. This oscillatory region is physically unrealistic in the

two-phase (liquid-gas coexistence) region observed in Andrews' experiments (the horizontal plateau). However, this S-shape qualitatively suggests the possibility of liquid-gas phase transition.

- **Maxwell's Equal Area Rule:** To correct this physical inconsistency and accurately represent the horizontal plateau, Maxwell's equal area rule is applied to the Van der Waals isotherms. This rule states that the horizontal line (constant pressure plateau) should be drawn such that the area above the line and below the theoretical Van der Waals curve (representing superheated liquid) is equal to the area below the line and above the theoretical Van der Waals curve (representing supercooled vapor). This correction provides a quantitative match for the saturation pressure and the liquid-vapor coexistence region.
- The Van der Waals equation therefore provides a qualitative (and with Maxwell's rule, a quantitative) explanation for the existence of liquid and gas phases, the critical point, and the deviations from ideal gas behavior observed in Andrew's experiments, primarily by incorporating the finite volume of molecules and attractive intermolecular forces.

Question 6:

(a) Obtain the coefficient of thermal conductivity (K) of a gas. Discuss the effect of temperature and molecular diameter on K . (7+5=12 marks)

- **Derivation of the coefficient of thermal conductivity (K) of a gas:**
 - Consider a gas enclosed between two parallel planes, say at $y = 0$ and $y = L$. Let there be a temperature gradient along the y -axis, with temperature T decreasing as y increases. Heat flows from the hotter region to the colder region.
 - Assume a uniform distribution of molecules in the x - z plane.

- Consider three planes at y_0 , $y_0 + \lambda$, and $y_0 - \lambda$, where λ is the mean free path of the molecules.
- Molecules passing through the plane at y_0 typically experienced their last collision at a distance of λ away.
- Molecules coming from $y_0 - \lambda$ have a higher average kinetic energy (due to higher temperature $T(y_0 - \lambda)$).
- Molecules coming from $y_0 + \lambda$ have a lower average kinetic energy (due to lower temperature $T(y_0 + \lambda)$).
- The rate of molecules crossing a unit area in one direction (e.g., in the +y direction) is $(1/6)n\bar{c}$, where n is the number density of molecules and \bar{c} is the average molecular speed. (Factor of 1/6 comes from assuming molecular motion is equally probable in 6 directions).
- The energy carried by molecules from the $y_0 - \lambda$ plane to the y_0 plane is approximately $(1/6)n\bar{c} \times \text{energy per molecule at } (y_0 - \lambda)$.
- The average energy per molecule is $C_{V'}T$, where $C_{V'}$ is the specific heat capacity per molecule at constant volume ($C_{V'} = C_V/N$, where N is number of molecules, or $C_{V'} = (f/2)k$ for f degrees of freedom).
- Heat current Q/A across the plane at y_0 is the net transfer of energy.
- Energy transferred from $y_0 - \lambda$ to y_0 : $(1/6)n\bar{c}C_{V'}T(y_0 - \lambda)$.
- Energy transferred from $y_0 + \lambda$ to y_0 : $(1/6)n\bar{c}C_{V'}T(y_0 + \lambda)$.
- Net heat flow Q per unit area per unit time: $Q = (1/6)n\bar{c}C_{V'}[T(y_0 - \lambda) - T(y_0 + \lambda)]$.
- Using Taylor expansion for small λ : $T(y_0 - \lambda) \approx T(y_0) - \lambda(dT/dy)|_{y_0}$
 $T(y_0 + \lambda) \approx T(y_0) + \lambda(dT/dy)|_{y_0}$
- So, $T(y_0 - \lambda) - T(y_0 + \lambda) \approx -2\lambda(dT/dy)$.
- $Q = (1/6)n\bar{c}C_{V'}[-2\lambda(dT/dy)]$

- $Q = -(1/3)n\bar{c}C_{V'}\lambda(dT/dy)$.
- Comparing with Fourier's Law of Heat Conduction: $Q = -K(dT/dy)$.
- Therefore, the coefficient of thermal conductivity $K = (1/3)n\bar{c}C_{V'}\lambda$.
- Substituting $\bar{c} = \sqrt{(8kT)/(\pi m)}$ and $\lambda = 1/(\sqrt{2}\pi d^2 n)$, and $C_{V'} = (f/2)k$ or simply $C_{V'} = C_V/N_A$ (molar specific heat divided by Avogadro's number), or just C_V per molecule.
- If $C_{V'}$ is specific heat capacity per unit mass (c_v), then $K = (1/3)\rho\bar{c}\lambda c_v$, where $\rho = nm$ (mass density).
- So, $K = (1/3)n\sqrt{(8kT)/(\pi m)}(C_{V'})(1/(\sqrt{2}\pi d^2 n))$.
- $K = (1/(3\sqrt{2}\pi d^2))\sqrt{(8kT)/(\pi m)}C_{V'}$.
- $K = (1/(3\sqrt{2}\pi d^2))\sqrt{8k/\pi m}C_{V'}\sqrt{T}$.
- It shows $K \propto \sqrt{T}$.
- If we use molar specific heat C_V and N_A (Avogadro's number), then $C_{V'} = C_V/N_A$.
- $K = (1/3)(N/V)\bar{c}(C_V/N)\lambda = (1/3)(N/V)(C_V/N)\bar{c}\lambda$. Here C_V is molar specific heat capacity.
- This formula can also be expressed in terms of viscosity η as $K = (1/2)C_V\eta/M$ (for monatomic gases). More generally, $K = \epsilon C_V\eta/M$ where ϵ is a factor close to 1.
- **Effect of temperature on K:**
 - From the derived expression $K = (1/(3\sqrt{2}\pi d^2))\sqrt{(8kT)/(\pi m)}C_{V'}$, we see that $K \propto \sqrt{T}$.

- As temperature increases, the average molecular speed \bar{c} increases. This leads to more frequent energy transport across planes and faster diffusion of kinetic energy.
- The number density n decreases with increasing temperature at constant pressure, but the increase in \bar{c} dominates.
- Therefore, the thermal conductivity of a gas **increases with increasing temperature**.

• **Effect of molecular diameter on K:**

- From the expression, $K \propto 1/d^2$, where d is the molecular diameter.
- A larger molecular diameter means a larger collision cross-section, which leads to a smaller mean free path ($\lambda \propto 1/d^2$).
- A shorter mean free path means molecules travel shorter distances between collisions, thus reducing the effective transport of energy.
- Therefore, the thermal conductivity of a gas **decreases with increasing molecular diameter**.

(b) Calculate the mean free path of the molecules of a gas of diameter 3 angstrom at STP. How does the mean free path change if the temperature is reduced to half of its original value and pressure is doubled. (6 marks)

• **Part 1: Calculate mean free path at STP.**

- Mean free path $\lambda = 1/(\sqrt{2}\pi d^2 n)$.
- At STP (Standard Temperature and Pressure):
 - $T = 0^\circ\text{C} = 273.15 \text{ K}$
 - $P = 1 \text{ atm} = 1.013 \times 10^5 \text{ Pa}$
- Molecular diameter $d = 3 \text{ angstrom} = 3 \times 10^{-10} \text{ m}$.
- We need the number density n . For an ideal gas, from $PV = nRT$, $n = P/(kT)$ per unit volume (if n is number of molecules, not moles).

- $n = P/(k_B T)$ where k_B is Boltzmann constant.
- $n = (1.013 \times 10^5 \text{ Pa}) / (1.38 \times 10^{-23} \text{ J/K} \times 273.15 \text{ K})$
- $n = (1.013 \times 10^5) / (3.779 \times 10^{-21})$
- $n \approx 2.68 \times 10^{25} \text{ molecules/m}^3$.
- Now calculate λ :
 - $\lambda = 1/(\sqrt{2} \times \pi \times (3 \times 10^{-10} \text{ m})^2 \times 2.68 \times 10^{25} \text{ m}^{-3})$
 - $\lambda = 1/(\sqrt{2} \times 3.14159 \times 9 \times 10^{-20} \text{ m}^2 \times 2.68 \times 10^{25} \text{ m}^{-3})$
 - $\lambda = 1/(1.4142 \times 3.14159 \times 9 \times 2.68 \times 10^5)$
 - $\lambda = 1/(107.03 \times 10^5)$
 - $\lambda = 1/(1.0703 \times 10^7)$
 - $\lambda \approx 9.34 \times 10^{-8} \text{ m}$ or 93.4 nm.
- **Part 2: How does the mean free path change if the temperature is reduced to half of its original value and pressure is doubled.**
 - The formula for mean free path is $\lambda = 1/(\sqrt{2}\pi d^2 n)$.
 - We know that $n = P/(kT)$.
 - So, $\lambda = kT/(\sqrt{2}\pi d^2 P)$.
 - Let the original conditions be T_1 and P_1 , and the new conditions be $T_2 = T_1/2$ and $P_2 = 2P_1$.
 - The new mean free path λ_2 will be:
 - $\lambda_2 = kT_2/(\sqrt{2}\pi d^2 P_2)$
 - $\lambda_2 = k(T_1/2)/(\sqrt{2}\pi d^2 (2P_1))$
 - $\lambda_2 = (1/4) \times (kT_1/(\sqrt{2}\pi d^2 P_1))$

- $\lambda_2 = (1/4)\lambda_1$.
- Therefore, if the temperature is reduced to half and the pressure is doubled, the mean free path will **become one-fourth of its original value**.

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