SECOND LAW OF THERMODYNAMICS AND ASSOCIATED CONCEPTS

NEED FOR A SECOND LAW

The first law of thermodynamics deals with the conservation of energy and describes energy transformations. However, it does not specify the direction in which a process can occur. For example, heat can flow from a hotter body to a colder body, but the first law alone does not forbid heat flowing from a colder body to a hotter body spontaneously. The second law introduces the concept of directionality and spontaneity in thermodynamic processes.

STATEMENTS OF THE SECOND LAW

The second law can be stated in several equivalent ways. The most common ones are:

- **Kelvin-Planck Statement:** It is impossible to construct a device that operates in a cycle and produces no effect other than the extraction of heat from a single reservoir and the performance of an equivalent amount of work. (This implies that no heat engine can be 100% efficient).
- **Clausius Statement:** It is impossible to construct a device that operates in a cycle and produces no effect other than the transfer of heat from a colder body to a hotter body. (This implies that a refrigerator requires work input to transfer heat from a colder to a hotter reservoir).

EQUIVALENCE OF STATEMENTS

The Kelvin-Planck and Clausius statements are equivalent. If one can be violated, the other can also be violated. Demonstrating the equivalence involves showing that if a device violating one statement exists, it can be combined with a device operating according to the other statement to create a cyclic device violating the first statement.

CONCEPT OF HEAT RESERVOIRS AND HEAT ENGINES

A **heat reservoir** is a body of matter (or a system) that can supply or absorb large amounts of energy with only negligible changes in its temperature. Examples include the atmosphere, large bodies of water, or furnaces maintained at a constant temperature.

A **heat engine** is a device that converts thermal energy into mechanical work. It operates in a cycle, absorbing heat from a high-temperature reservoir, converting a portion of it into work, and rejecting the remaining heat to a low-temperature reservoir.

CARNOT CYCLE

The Carnot cycle is a theoretical thermodynamic cycle that describes the most efficient possible cycle for converting heat into work between two heat reservoirs. It consists of four reversible processes:

1. Isothermal expansion at high temperature (T_H).
2. Adiabatic expansion.
3. Isothermal compression at low temperature (T_L).
4. Adiabatic compression.

This cycle is ideal and serves as a benchmark for real-world engines.

CARNOT ENGINE AND REFRIGERATOR

A **Carnot engine** is a hypothetical heat engine that operates on the Carnot cycle. Its efficiency is given by:

$$\eta_{Carnot} = 1 - (T_L / T_H)$$

where T_L and T_H are the absolute temperatures of the cold and hot reservoirs, respectively.

A **Carnot refrigerator** is a hypothetical refrigerator that operates on the reverse Carnot cycle. It absorbs heat from a cold reservoir and rejects it to a hot reservoir, requiring work input. Its performance is measured by the Coefficient of Performance (COP):

$$COP_{Carnot\_refrigerator} = T_L / (T_H - T_L)$$

CARNOT'S THEOREM

Carnot's theorem states two things:

1. No engine operating between two heat reservoirs can be more efficient than a Carnot engine operating between the same two reservoirs.
2. All reversible engines operating between the same two heat reservoirs have the same efficiency, which is the Carnot efficiency.

VALUES OF §DQ/T AND CLAUSIUS INEQUALITY

For any cyclic process, the integral of `dQ/T` around the cycle (where `dQ` is the heat added and T is the absolute temperature at which it is added) is:

- For a reversible cycle: `§(dQ/T)_rev = 0`
- For an irreversible cycle: `§(dQ/T)_irrev < 0`

This leads to the **Clausius Inequality**: `§(dQ/T) ≤ 0`, with equality holding for reversible cycles.

PHYSICAL CONCEPT OF ENTROPY

Entropy (S) is a thermodynamic property that is a measure of the disorder or randomness of a system. It is a state function, meaning its value depends only on the current state of the system, not on how it reached that state.

Entropy is often described as a measure of the microscopic disorder of the system. A more disordered system has higher entropy. For example, a gas filling a container has higher entropy than the same gas compressed into a small volume.

ENTROPY CHANGES OF SYSTEMS AND SURROUNDINGS

The change in entropy of the universe (system + surroundings) for any process is:

- For a reversible process: `ΔS_universe = ΔS_system + ΔS_surroundings = 0`

- For an irreversible process: `ΔS_universe = ΔS_system + ΔS_surroundings > 0`

This implies that the total entropy of an isolated system can never decrease over time, and it remains constant if only reversible processes occur.

ENTROPY AND UNAVAILABLE WORK

Entropy is also related to the concept of unavailable energy. In any irreversible process, some energy becomes unavailable to do useful work. This unavailable energy is directly related to the increase in entropy of the universe. The maximum useful work obtainable from a system is reduced by the term `T_0 * ΔS_universe`, where `T_0` is the temperature of the surroundings.

TEMPERATURE–ENTROPY (T-S) DIAGRAM

A T-S diagram plots absolute temperature (T) on the y-axis and entropy (S) on the x-axis. For a reversible process, the area under the curve T dS represents the heat transferred:

`Q_rev = ∫ T dS`

This diagram is useful for visualizing reversible cycles and calculating heat transfers and entropy changes.

USEFUL WORK AND THERMODYNAMIC POTENTIALS

Useful work is the work done by a system, excluding the work done against the surroundings (e.g., expansion work at constant pressure). Thermodynamic potentials are state functions that help determine the spontaneity and equilibrium of processes under different conditions.

GIBBS AND HELMHOLTZ FUNCTIONS

Two important thermodynamic potentials are:

- **Helmholtz Free Energy (A):** `A = U - TS`, where U is internal energy. It represents the maximum work obtainable from a system at constant temperature and volume. `ΔA ≤ 0` for spontaneous processes at constant T, V.
- **Gibbs Free Energy (G):** `G = H - TS`, where H is enthalpy. It represents the maximum useful work (non-expansion work) obtainable from a system at constant temperature and pressure. `ΔG ≤ 0` for spontaneous processes at constant T, P.

CHANGES AT CONSTANT TEMPERATURE AND PRESSURE

For processes occurring at constant temperature (T) and pressure (P):

- Spontaneity is determined by the change in Gibbs Free Energy (ΔG).
- If `ΔG < 0`, the process is spontaneous.
- If `ΔG > 0`, the process is non-spontaneous (reverse process is spontaneous).
- If `ΔG = 0`, the system is at equilibrium.

APPLICATION TO ELECTRIC WORK

The change in Gibbs Free Energy is also related to maximum electrical work obtainable from electrochemical cells (galvanic cells). For a reversible process at constant T and P:

```
ΔG = W_useful_max = -nFE
```

where n is the number of moles of electrons transferred, F is Faraday's constant, and E is the cell potential.

CRITERIA FOR SPONTANEITY AND EQUILIBRIUM

Summary of criteria:

- **Constant T, V:** `ΔA ≤ 0` (Spontaneous if < 0, Equilibrium if = 0).
- **Constant T, P:** `ΔG ≤ 0` (Spontaneous if < 0, Equilibrium if = 0).

- **Isolated System (Constant U, V):** $\Delta S \geq 0$ (Spontaneous if > 0, Equilibrium if = 0).

GIBBS-HELMHOLTZ EQUATION

The Gibbs-Helmholtz equation relates the change in Gibbs free energy to enthalpy and temperature:

$$(\partial(\Delta G/T)/\partial T)_P = -\Delta H/T^2$$

This equation is useful for determining how ΔG changes with temperature and for calculating thermodynamic properties.

GIBBS FREE ENERGY AND BIOLOGICAL SYSTEMS/PHASE TRANSITIONS

In biological systems, ΔG determines whether biochemical reactions will proceed spontaneously. For phase transitions (e.g., melting, boiling), equilibrium is reached when the Gibbs free energy of the two phases is equal, i.e., $\Delta G = 0$ at the transition temperature and pressure.

MAXWELL'S RELATIONS

Maxwell's relations are a set of four equations derived from the fundamental thermodynamic relations (based on U, H, A, G). They relate partial derivatives of thermodynamic properties. For example, one relation is:

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

These relations are crucial for calculating thermodynamic properties from experimental data.

JOULE-THOMSON EXPERIMENT AND CONSEQUENCES

The Joule-Thomson experiment measures the temperature change of a real gas when it is forced through a porous plug or valve (throttling process) at constant enthalpy. For ideal gases, there is no temperature change. Real gases show a temperature change that depends on their properties.

INVERSION TEMPERATURE

The **inversion temperature** is the temperature at which the Joule-Thomson effect changes sign. Below the inversion temperature, gases cool upon throttling; above it, they heat up. For many gases, the inversion temperature is significantly above room temperature.

JOULE-THOMSON COEFFICIENT FOR A VAN DER WAALS GAS

The Joule-Thomson coefficient (μ_{JT}) is defined as $\mu_{JT} = (\partial T/\partial P)_H$. For a van der Waals gas, the `μ_JT` can be derived in terms of the gas constants and temperature, showing its deviation from ideal gas behavior.

GENERAL HEAT CAPACITY RELATIONS

Heat capacity relations connect heat capacities at constant volume (C_v) and constant pressure (C_p) to other thermodynamic properties. For example:

$$C_p - C_v = T (\partial P/\partial T)_V (\partial V/\partial T)_P$$

and for ideal gases, $C_p - C_v = nR$.

NUMERICAL PROBLEMS

This section would contain a variety of numerical problems designed to test understanding of the concepts covered. Examples include:

- Calculating the efficiency of heat engines and COP of refrigerators.
- Determining entropy changes for various processes (ideal gas expansion, phase change, mixing).
- Calculating Gibbs and Helmholtz free energy changes for reactions and phase transitions.
- Applying Maxwell's relations or Joule-Thomson coefficient for specific gases.

Problem 1: A heat engine operates between $500\ \mathrm{K}$ and $300\ \mathrm{K}$. If it is a Carnot engine, calculate its efficiency. If it has an efficiency of 30%, how much heat is rejected to the cold reservoir for every 1000 J of heat absorbed from the hot reservoir?

Problem 2: Calculate the entropy change when 1 kg of water at 25°C is converted to steam at 100°C and 1 atm pressure. (Latent heat of vaporization = 2257 kJ/kg).

Problem 3: For a certain gas, the Joule-Thomson coefficient is `μ_JT = (2a/RT - b)`, where a and b are van der Waals constants. Calculate the inversion temperature for this gas.

Problem 4: Determine the change in Gibbs free energy for a reaction with `ΔH = -50 kJ/mol` and `ΔS = -100 J/(mol·K)` at 298 K. Is the reaction spontaneous?