

Thermodynamics of Fluids

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Unit 1 – Intro to Fluid Thermodynamics

1.1 Fundamental concepts and definitions

Thermodynamics explores how energy moves and changes form. It's all about understanding heat, work, and the properties of substances like temperature and pressure. These concepts are key to grasping how fluids behave and interact with their surroundings.

This section lays the groundwork for the rest of the chapter. It introduces basic ideas like equilibrium, ideal gases, and fluid characteristics that we'll build on as we dive deeper into the thermodynamics of fluids.

Thermodynamic Fundamentals

Core Concepts

- Thermodynamics studies the interconversion of heat and other forms of energy
- Energy represents the capacity to do work and exists in various forms (kinetic, potential, thermal, electrical, chemical, nuclear)
- Heat refers to energy transferred from one system to another due to a temperature difference between them
- Work occurs when a force acts upon an object to cause a displacement and can be represented as $W = \int F \cdot ds$

Equilibrium

- Equilibrium describes a state where a system experiences no changes when it is isolated from its surroundings
- In thermodynamic equilibrium, there are no unbalanced potentials (or driving forces) within the system
- Systems in equilibrium must satisfy three conditions:
 - Mechanical equilibrium: no unbalanced forces
 - Thermal equilibrium: no temperature differences
 - Chemical equilibrium: no chemical potential differences (or ongoing chemical reactions)
- Equilibrium states serve as a starting point for solving many thermodynamic problems and analyzing processes

Fluid Properties

Fluid Characteristics

- A fluid refers to a substance that continuously deforms under an applied shear stress, encompassing both liquids and gases
- Fluids take the shape of their container and cannot withstand shear stresses in static equilibrium
- Fluids exhibit properties such as density, viscosity, and compressibility that influence their behavior and flow characteristics

- Phase describes the distinct forms that a substance can exist in (solid, liquid, or gas) depending on the conditions of temperature and pressure

Temperature and Pressure

- Temperature represents a measure of the average kinetic energy of the particles in a substance
- Absolute temperature scales (Kelvin, Rankine) have their zero point at absolute zero, where molecular motion theoretically ceases
- Pressure is defined as the force per unit area exerted by a fluid on its surroundings, typically expressed in units of Pascals (Pa) or atmospheres (atm)
- Hydrostatic pressure in a fluid at rest increases linearly with depth due to the weight of the fluid column above $P = \rho gh$

Ideal Gas Model

Ideal Gas Assumptions and Behavior

- An ideal gas consists of a large number of identical particles that occupy a negligible volume compared to the container
- Ideal gas particles have no intermolecular forces (except during elastic collisions) and possess random motion
- The behavior of an ideal gas can be described by the ideal gas law $PV = nRT$, relating pressure (P), volume (V), amount of substance (n), universal gas constant (R), and absolute temperature (T)
- Real gases approach ideal gas behavior at low pressures and high temperatures, where intermolecular forces become less significant
- Ideal gas assumptions simplify the analysis of gas behavior and enable the derivation of useful relationships (Boyle's law, Charles' law, Gay-Lussac's law)

1.2 Thermodynamic systems and processes

Thermodynamic systems and processes are the building blocks of fluid behavior. We'll explore how energy and matter flow within different system types, and how properties like temperature and pressure change during various processes.

Understanding these concepts is crucial for analyzing real-world applications. From car engines to power plants, grasping how systems interact with their surroundings and undergo changes is key to mastering thermodynamics of fluids.

System Types

Open, Closed, and Isolated Systems

- Open system can exchange both energy and matter with its surroundings (a car engine)
- Closed system can exchange energy but not matter with its surroundings (a sealed piston-cylinder device)
- Isolated system cannot exchange either energy or matter with its surroundings (an insulated, sealed container)

- Most real-world systems are open systems since they interact with their environment
- Analyzing a system often involves defining the system boundary, which separates the system from its surroundings

System Properties and Equilibrium

- Thermodynamic properties describe the state of a system (temperature, pressure, volume, internal energy)
- Intensive properties are independent of the system size (temperature, pressure)
- Extensive properties depend on the size of the system (volume, mass, internal energy)
- Thermodynamic equilibrium occurs when a system's properties remain constant over time
- Systems in equilibrium have uniform properties throughout and no net flow of energy or matter across the system boundary

Thermodynamic Processes

Quasi-static and Reversible Processes

- Quasi-static process occurs slowly enough that the system remains infinitesimally close to equilibrium at all times
- Reversible process is a quasi-static process where the system and surroundings can be restored to their original states by reversing the process
- Reversible processes are idealized and serve as a limit for real processes
- Most real processes are irreversible due to friction, heat transfer, and other dissipative effects

Isothermal, Adiabatic, Isobaric, and Isochoric Processes

- Isothermal process occurs at constant temperature (a system in contact with a large thermal reservoir)
- Adiabatic process occurs without heat transfer between the system and surroundings (rapid compression or expansion of a gas)
- Isobaric process occurs at constant pressure (heating a gas in a piston-cylinder device with a constant external force)
- Isochoric process, also known as an isovolumetric process, occurs at constant volume (heating a gas in a rigid container)
- Many real processes can be approximated as a combination of these idealized processes
- Understanding these processes helps in analyzing and designing thermodynamic systems (heat engines, refrigerators, power plants)

1.3 Thermodynamic properties and state variables

Thermodynamic properties and state variables are key to understanding fluid behavior. They help us describe and predict how fluids react to changes in temperature, pressure, and volume. These concepts are crucial for analyzing energy systems and solving real-world engineering problems.

Intensive properties like pressure and temperature don't depend on the amount of fluid, while extensive properties like volume do. State variables describe a system's condition, and specific heat capacity tells us how much energy it takes to heat something up. These ideas form the foundation for deeper thermodynamic analysis.

Properties and State Variables

Types of Properties

- Intensive properties
- Properties that are independent of the amount of matter present in a system
- Examples include pressure, temperature, and density
- Extensive properties
- Properties that depend on the amount of matter present in a system
- Examples include volume, mass, and total energy
- Can be converted to intensive properties by dividing by the mass or mole number of the system

State Variables and Specific Heat Capacity

- State variables
- Variables that describe the thermodynamic state of a system
- Common state variables include pressure, temperature, volume, and composition
- Knowledge of state variables allows for the determination of other thermodynamic properties
- Specific heat capacity
- Measure of the amount of heat required to raise the temperature of a unit mass of a substance by one degree
- Varies depending on the substance and the conditions (constant pressure or constant volume)
- Plays a crucial role in heat transfer calculations and thermodynamic analysis

Thermodynamic Properties

Pressure, Temperature, and Volume

- Pressure
- Force per unit area exerted by a fluid on its surroundings
- Measured in units such as pascals (Pa), bars, or atmospheres (atm)
- Plays a crucial role in determining the behavior and properties of fluids
- Temperature
- Measure of the average kinetic energy of the particles in a system
- Determines the direction of heat transfer between systems

- Measured in units such as Kelvin (K) or degrees Celsius (°C)
- Volume
- Amount of space occupied by a system
- Can be expressed as total volume or specific volume (volume per unit mass)
- Changes in volume are often associated with work done by or on the system

Energy and Entropy

- Internal energy
- Total kinetic and potential energy of the particles within a system
- Depends on the temperature, composition, and intermolecular forces of the system
- Changes in internal energy are associated with heat transfer and work
- Enthalpy
- Sum of the internal energy and the product of pressure and volume ($H = U + PV$)
- Represents the total heat content of a system
- Changes in enthalpy are important in processes involving heat transfer at constant pressure
- Entropy
- Measure of the disorder or randomness of a system
- Always increases in spontaneous processes and remains constant in reversible processes
- Plays a key role in determining the direction and spontaneity of thermodynamic processes

Equation of State

Relating Thermodynamic Properties

- Equation of state
- Mathematical relationship between state variables (pressure, temperature, volume, and composition)
- Allows for the prediction of the behavior of a system under different conditions
- Examples include the ideal gas law ($PV = nRT$) and the van der Waals equation
- Different equations of state are used for different types of substances (gases, liquids, solids) and different ranges of conditions
- Knowledge of the appropriate equation of state is essential for accurate thermodynamic calculations and analysis

1.4 Units and dimensions in thermodynamics

Units and dimensions are the backbone of thermodynamics. They help us measure and compare physical quantities like pressure, temperature, and energy. Without them, we'd be lost in a sea of numbers with no context.

In this section, we'll look at different measurement systems and units for key thermodynamic properties. We'll see how SI units provide a standardized way to communicate scientific data across the globe.

Measurement Systems

International System of Units (SI)

- Internationally standardized metric system used in science, engineering, and commerce
- Consists of seven base units (meter, kilogram, second, ampere, kelvin, mole, candela) from which all other units are derived
- Prefixes (milli, centi, kilo, mega) used to indicate orders of magnitude
- Ensures consistency and ease of conversion between units across different fields and countries

Imperial Units

- System of measurement used primarily in the United States and a few other countries
- Based on arbitrary units (foot, pound, gallon) that lack the coherent relationship found in SI units
- Conversions between units often require memorization or reference tables
- Gradually being phased out in favor of SI units to facilitate international trade and scientific collaboration

Pressure Units

Pascal (Pa)

- SI unit for pressure, defined as one newton per square meter (N/m^2)
- Named after Blaise Pascal, a French mathematician, physicist, and philosopher
- Commonly used in scientific and engineering applications (atmospheric pressure, material stress)
- Multiples such as kilopascal (kPa) and megapascal (MPa) are often used for convenience

Bar

- Non-SI unit of pressure, defined as 100,000 pascals (100 kPa)
- Approximately equal to the atmospheric pressure at sea level (1.01325 bar)
- Commonly used in meteorology, scuba diving, and industrial settings (tire pressure, gas cylinder pressure)
- Millibar (mbar) is a smaller unit, equal to one-thousandth of a bar, often used in weather forecasts

Temperature Units

Kelvin (K)

- SI unit for thermodynamic temperature, named after Lord Kelvin, a British mathematician and physicist
- Defined as $1/273.16$ of the thermodynamic temperature of the triple point of water

- Zero kelvin (absolute zero) is the lowest possible temperature, at which all molecular motion ceases
- Used in scientific applications where absolute temperature is essential (thermodynamics, astrophysics)

Celsius (°C)

- Metric unit for temperature, widely used in everyday life and scientific applications
- Defined such that 0°C is the freezing point and 100°C is the boiling point of water at standard atmospheric pressure
- Easily convertible to Kelvin: $T(K) = T(^{\circ}C) + 273.15$
- Commonly used in weather reports, cooking, and medical settings (body temperature)

Energy and Power Units

Joule (J)

- SI unit for energy, work, and heat, named after James Prescott Joule, an English physicist
- Defined as the work done when a force of one newton is applied over a distance of one meter (1 J = 1 N·m)
- Used to quantify various forms of energy (kinetic, potential, thermal, electrical)
- Multiples such as kilojoule (kJ) and megajoule (MJ) are often used for convenience (food calories, explosives)

Watt (W)

- SI unit for power, named after James Watt, a Scottish inventor and engineer
- Defined as one joule per second (1 W = 1 J/s), representing the rate of energy transfer or consumption
- Used to quantify the power of electrical devices, mechanical engines, and solar panels
- Multiples such as kilowatt (kW) and megawatt (MW) are often used for larger-scale applications (household appliances, power plants)

Unit 2 – Properties of Pure Substances

2.1 Phase behavior and phase diagrams

Phase transitions are key to understanding how substances change states. Temperature and pressure play crucial roles, influencing whether a substance is solid, liquid, or gas. Knowing these basics helps predict how materials behave in different conditions.

Critical and triple points are special cases in phase behavior. The critical point marks where liquid and gas become indistinguishable, while the triple point is where all three phases coexist. These concepts are vital for many industrial and scientific applications.

Phase Transitions

Types of Phase Transitions

- Phase refers to a state of matter with uniform physical properties (solid, liquid, or gas)
- Sublimation occurs when a substance transitions directly from solid to gas without passing through the liquid phase (dry ice)
- Melting happens when a solid substance changes to a liquid state due to an increase in temperature (ice melting into water)
- Boiling takes place when a liquid transitions to a gas at a specific temperature and pressure (water boiling into steam)

Factors Influencing Phase Transitions

- Temperature plays a crucial role in determining the phase of a substance as it affects the kinetic energy of molecules
- Pressure also influences phase transitions by altering the equilibrium between phases (lower pressure promotes evaporation)
- The nature of intermolecular forces within a substance affects its phase behavior and transition points (stronger forces lead to higher melting and boiling points)
- The rate of heat transfer to or from a substance determines the speed at which phase transitions occur (rapid heating leads to faster melting)

Critical Points

Critical Point and Its Significance

- Critical point represents the highest temperature and pressure at which a substance can exist as a liquid and gas in equilibrium
- At the critical point, the properties of the liquid and gas phases become identical, and the phase boundary disappears (carbon dioxide at 31.1°C and 73.8 bar)
- Beyond the critical point, a substance enters a supercritical state where it exhibits properties of both a liquid and a gas (high density and low viscosity)

- Supercritical fluids have unique solvent properties and are used in various applications (supercritical CO₂ for decaffeination and dry cleaning)

Triple Point and Its Implications

- Triple point refers to the specific temperature and pressure at which all three phases (solid, liquid, and gas) of a substance can coexist in equilibrium
- At the triple point, the vapor pressure of the solid and liquid phases are equal (water's triple point at 0.01°C and 611.73 Pa)
- The triple point is a unique and invariant property of a pure substance and is used as a reference point for temperature scales (Kelvin scale defines 273.16 K as the triple point of water)
- Understanding the triple point is essential for processes involving phase transitions and for calibrating temperature measurement devices

Phase Diagrams

Components and Interpretation of Phase Diagrams

- Phase diagram graphically represents the equilibrium relationships between the solid, liquid, and gas phases of a substance as a function of temperature and pressure
- Vapor pressure curve shows the equilibrium pressure at which a liquid and its vapor coexist at different temperatures (water's vapor pressure curve from triple point to critical point)
- Saturation refers to the state of a system where the vapor pressure equals the surrounding pressure, and the liquid and vapor phases are in equilibrium (saturated steam in power plants)
- The melting curve represents the equilibrium between solid and liquid phases, while the sublimation curve depicts the equilibrium between solid and gas phases

Applications and Limitations of Phase Diagrams

- Phase diagrams are essential tools for understanding and predicting the behavior of substances under different conditions (designing refrigeration systems and heat exchangers)
- They help determine the operating conditions for processes involving phase transitions, such as distillation, crystallization, and drying (optimizing separation processes in chemical industries)
- Phase diagrams also provide insights into the stability and metastability of phases, which is crucial for material processing and storage (preventing unwanted phase changes in pharmaceuticals)
- However, phase diagrams are limited to pure substances and do not account for the presence of impurities or mixtures, which can alter the phase behavior significantly (freezing point depression and boiling point elevation in solutions)

2.2 P-v-T behavior of pure substances

Pressure, volume, and temperature are the building blocks of thermodynamics. These properties help us understand how substances behave under different conditions. Knowing how they interact is key to grasping the bigger picture of pure substances.

Constant property processes like isothermal, isobaric, and isochoric give us a way to analyze substance behavior. By keeping one property constant, we can see how the others change. This helps us predict and

control substance behavior in real-world applications.

Thermodynamic Properties

Pressure, Volume, and Temperature

- Pressure (P) represents the force per unit area exerted by a fluid
- Measured in units such as pascals (Pa), bars, or pounds per square inch (psi)
- Atmospheric pressure at sea level is approximately 101,325 Pa or 1 atm
- Specific volume (V) is the volume occupied by a unit mass of a substance
- Reciprocal of density (ρ) and is expressed as $v = 1/\rho$
- Commonly measured in units such as cubic meters per kilogram (m³/kg) or cubic feet per pound (ft³/lb)
- Temperature (T) is a measure of the average kinetic energy of the particles in a substance
- Expressed in units of Kelvin (K) or degrees Celsius (°C) for SI units and Rankine (°R) or Fahrenheit (°F) for English units
- Absolute zero is the lowest possible temperature, corresponding to 0 K or -273.15 °C

Constant Property Processes

Isothermal, Isobaric, and Isochoric Processes

- Isotherms are processes that occur at constant temperature
- On a P-v diagram, isotherms appear as hyperbolic curves for an ideal gas
- For an ideal gas undergoing an isothermal process, the product of pressure and volume remains constant ($PV = \text{constant}$)
- Isobars are processes that occur at constant pressure
- On a P-v diagram, isobars appear as horizontal lines
- During an isobaric process, the volume of a substance changes while the pressure remains constant
- Isochores are processes that occur at constant volume
- On a P-v diagram, isochores appear as vertical lines
- During an isochoric process, the pressure of a substance changes while the volume remains constant

Material Behavior

Compressibility and Thermal Expansion

- Compressibility is a measure of a substance's ability to change its volume in response to a change in pressure
- Isothermal compressibility (β_T) is defined as $\beta_T = -\frac{1}{v} \left(\frac{\partial v}{\partial P} \right)_T$
- Substances with high compressibility (gases) experience significant volume changes with pressure, while those with low compressibility (liquids and solids) experience minimal volume changes

- Thermal expansion is the tendency of a substance to change its volume in response to a change in temperature
- Volumetric thermal expansion coefficient (α_v) is defined as $\alpha_v = \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_p$
- Most substances expand when heated and contract when cooled, with gases exhibiting the highest thermal expansion, followed by liquids and solids
- Water is an exception, as it expands when cooled from 4 °C to 0 °C due to its unique molecular structure

2.3 Thermodynamic data tables and their use

Thermodynamic data tables are essential tools for engineers and scientists working with pure substances. They provide crucial information about properties like enthalpy, entropy, and specific volume at various temperatures and pressures.

These tables help solve real-world problems involving phase changes, heat transfer, and energy conversion. By using interpolation techniques and understanding concepts like quality, engineers can accurately analyze complex thermodynamic systems and processes.

Thermodynamic Property Tables

Saturation Tables

- Provide thermodynamic properties of a substance at saturation conditions, where the liquid and vapor phases coexist in equilibrium
- Organized by saturation temperature or pressure, allowing users to find properties at specific saturation states
- Include properties such as specific volume, specific enthalpy, and specific entropy for both saturated liquid and saturated vapor states
- Enable users to determine the boiling point or condensation point of a substance at a given pressure or temperature
- Crucial for analyzing phase change processes, such as boiling, condensation, and evaporation (water boiling in a kettle, steam condensing in a power plant condenser)

Superheated Vapor Tables

- Contain thermodynamic properties of a substance in the superheated vapor state, where the vapor is at a temperature higher than its saturation temperature at a given pressure
- Arranged by pressure and temperature, allowing users to find properties at specific superheated vapor states
- Include properties such as specific volume, specific enthalpy, and specific entropy for the superheated vapor
- Essential for analyzing processes involving superheated vapor, such as expansion in a steam turbine or compression in a refrigeration cycle (superheated steam in a power plant, superheated refrigerant in an air conditioning system)

Compressed Liquid Tables

- Provide thermodynamic properties of a substance in the compressed liquid state, where the liquid is at a pressure higher than its saturation pressure at a given temperature
- Organized by pressure and temperature, allowing users to find properties at specific compressed liquid states
- Include properties such as specific volume, specific enthalpy, and specific entropy for the compressed liquid
- Useful for analyzing processes involving compressed liquids, such as pumping or throttling (water in a high-pressure pump, refrigerant in a throttling valve)

Property Evaluation and Interpolation

Interpolation Techniques

- Linear interpolation is a simple method for estimating properties between two known data points in a table, assuming a linear relationship between the properties and the independent variable (pressure or temperature)
- Double interpolation is required when the desired state falls between the values provided in both the pressure and temperature columns of a table, involving interpolation in one direction followed by interpolation in the other direction
- Accuracy of interpolation depends on the spacing of data points in the table and the linearity of the property relationships (closer data points and more linear relationships yield better accuracy)
- Interpolation is necessary because tables provide properties at discrete state points, while many thermodynamic problems involve states that fall between the tabulated values (estimating properties at intermediate pressures or temperatures)

Quality and Phase Equilibrium

- Quality, denoted by X , represents the mass fraction of vapor in a two-phase mixture of liquid and vapor in equilibrium
- Saturated liquid has a quality of 0, while saturated vapor has a quality of 1; states with $0 < x < 1$ are two-phase mixtures
- Properties of a two-phase mixture can be calculated using quality and the properties of saturated liquid and saturated vapor at the given pressure or temperature: $p_{mixture} = (1 - X) \cdot p_f + X \cdot p_g$
- Quality is used to determine the state and properties of a substance during phase change processes, such as evaporation or condensation (calculating the enthalpy of a two-phase mixture in a partially filled steam boiler)

Thermodynamic Properties

Specific Enthalpy

- Specific enthalpy, denoted by h , is the enthalpy per unit mass of a substance, representing the total energy content (internal energy plus flow work) per unit mass

- Enthalpy is a state function, meaning its value depends only on the current state of the system and not on the path taken to reach that state
- Changes in specific enthalpy are important for analyzing heat transfer and work interactions in thermodynamic processes (calculating the energy required to heat water from room temperature to boiling point)
- Specific enthalpy values are provided in thermodynamic property tables for various states, such as saturated liquid, saturated vapor, and superheated vapor (steam tables)

Specific Entropy

- Specific entropy, denoted by S , is the entropy per unit mass of a substance, representing the amount of energy dispersed or unavailable for useful work per unit mass
- Entropy is a state function and a measure of the disorder or randomness of a system; it always increases in real processes due to irreversibilities
- Changes in specific entropy are used to determine the direction of heat transfer and to assess the reversibility of thermodynamic processes (comparing the entropy change of a reversible and irreversible compression)
- Specific entropy values are provided in thermodynamic property tables for various states, such as saturated liquid, saturated vapor, and superheated vapor (refrigerant tables)

Internal Energy

- Internal energy, denoted by U , is the energy associated with the microscopic components of a system, such as the kinetic and potential energies of molecules
- Specific internal energy is the internal energy per unit mass of a substance
- Changes in internal energy are related to heat transfer and work interactions through the first law of thermodynamics: $\Delta U = Q - W$
- Internal energy is a state function, and its value depends only on the current state of the system, not on the path taken to reach that state (comparing the internal energy change of a gas undergoing compression in a piston-cylinder device)
- Specific internal energy values can be calculated from specific enthalpy and specific volume data provided in thermodynamic property tables: $u = h - pv$

2.4 Ideal and real gas behavior

Gas behavior is a crucial concept in thermodynamics. Ideal gases follow simple laws, but real gases deviate due to molecular interactions and volume. Understanding these differences helps predict how gases behave under various conditions.

Real gas equations, like Van der Waals and virial equations, account for these deviations. They introduce factors like compressibility and reduced properties, which are essential for accurately describing gas behavior in real-world applications.

Ideal Gas Behavior

Ideal Gas Law and Its Assumptions

- Ideal gas law relates pressure, volume, temperature, and amount of gas ($PV = nRT$)
- Assumes gas molecules have negligible volume compared to the container
- Assumes no intermolecular forces between gas molecules
- Assumes elastic collisions between molecules and container walls
- Assumes average kinetic energy of molecules is proportional to absolute temperature

Deviations from Ideal Behavior

- Real gases deviate from ideal behavior at high pressures and low temperatures
- Deviations occur due to finite volume of gas molecules (affects volume available for motion)
- Deviations also caused by intermolecular forces between gas molecules (affects pressure)
- Critical point is the highest temperature and pressure at which a substance can exist as a liquid and gas in equilibrium
- Compressibility factor (Z) quantifies the deviation of a real gas from ideal behavior ($Z = \frac{PV}{nRT}$)

Real Gas Equations of State

Van der Waals Equation

- Modifies ideal gas law to account for finite molecular volume and intermolecular forces
- Introduces constants a (accounts for intermolecular attraction) and b (accounts for molecular volume)
- Van der Waals equation: $\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$
- Predicts the existence of a critical point and liquid-vapor equilibrium
- Provides a more accurate description of real gas behavior than the ideal gas law

Virial Equation

- Expresses the compressibility factor as a power series in terms of pressure or volume
- Virial equation: $Z = 1 + \frac{B(T)}{V} + \frac{C(T)}{V^2} + \dots$
- $B(T)$ and $C(T)$ are the second and third virial coefficients, which depend on temperature
- Virial coefficients account for the cumulative effect of intermolecular interactions
- Truncated virial equations (e.g., truncated after the second term) are often used for simplicity

Real Gas Properties

Compressibility Factor and Its Applications

- Compressibility factor (Z) is the ratio of the actual volume of a gas to the volume predicted by the ideal gas law at the same pressure and temperature
- $Z = 1$ for an ideal gas, $Z < 1$ for a gas with dominant intermolecular attractions, and $Z > 1$ for a gas with dominant repulsive interactions
- Compressibility factor is used to correct the ideal gas law for real gas behavior ($PV = ZnRT$)
- Z can be determined experimentally or estimated using generalized compressibility charts (Nelson-Oberster charts)

Reduced Properties and the Corresponding States Principle

- Reduced properties are dimensionless quantities that relate the actual properties of a gas to its critical properties
- Reduced pressure: $P_r = \frac{P}{P_c}$, reduced temperature: $T_r = \frac{T}{T_c}$, reduced volume: $V_r = \frac{V}{V_c}$
- The corresponding states principle states that all gases, when compared at the same reduced conditions, have approximately the same compressibility factor
- This principle allows the estimation of real gas properties using generalized charts or equations with reduced properties
- The law of corresponding states is useful for predicting the behavior of gases when limited experimental data is available

Unit 3 – Equations of State

3.1 Ideal gas equation and its limitations

The ideal gas equation is a cornerstone of thermodynamics, relating pressure, volume, temperature, and amount of gas. It's crucial for understanding gas behavior, but it's not perfect. Real gases deviate from ideal behavior, especially at high pressures and low temperatures.

To account for these deviations, we use the compressibility factor. This helps modify the ideal gas law for real gases, considering intermolecular forces and finite molecular volume. Understanding these limitations is key to accurately predicting and analyzing gas behavior in various conditions.

Ideal Gas Law and its Variables

Equation and Components

- Ideal gas law relates pressure, volume, temperature, and amount of gas $PV = nRT$
- Pressure (P) force per unit area exerted by gas molecules colliding with container walls measured in pascals (Pa) or atmospheres (atm)
- Volume (V) space occupied by the gas typically measured in cubic meters (m^3) or liters (L)
- Temperature (T) average kinetic energy of gas molecules must be expressed in Kelvin (K) for ideal gas law calculations
- Gas constant (R) proportionality constant specific to the gas being studied has a value of $8.314 \frac{J}{mol \cdot K}$ for ideal gases

Relationships and Applications

- Directly proportional relationships between pressure and temperature as well as moles and volume $P \propto T$ and $n \propto V$ when other variables held constant
- Inversely proportional relationship between pressure and volume $P \propto \frac{1}{V}$ when temperature and moles held constant (Boyle's Law)
- Can be used to calculate changes in gas properties during processes like isothermal compression ($T = \text{constant}$) or isobaric expansion ($P = \text{constant}$)
- Enables determination of molar mass and density of gases by measuring P , V , T , and mass of a gas sample

Deviations from Ideal Gas Behavior

Compressibility Factor

- Compressibility factor (Z) ratio of actual molar volume of a gas to the molar volume predicted by the ideal gas law at the same temperature and pressure $Z = \frac{V_{\text{actual}}}{V_{\text{ideal}}}$
- Quantifies the extent of deviation from ideal gas behavior $Z = 1$ for an ideal gas and $Z \neq 1$ for a real gas

- Depends on the specific gas, temperature, and pressure with greater deviations occurring at high pressures and low temperatures
- Can be used to modify the ideal gas law for real gases $PV = ZnRT$ to account for non-ideal behavior

Real Gas Behavior and Intermolecular Forces

- Real gases exhibit non-ideal behavior due to the presence of intermolecular forces and finite molecular volume which are neglected in the ideal gas model
- Attractive forces (van der Waals forces) between molecules cause real gases to have lower pressure and molar volume than predicted by the ideal gas law
- Repulsive forces between molecules at high pressures cause real gases to have higher pressure and molar volume than predicted by the ideal gas law
- The degree of deviation depends on the strength of intermolecular forces specific to each gas with larger, more polarizable molecules (CO₂) exhibiting greater deviations than smaller, non-polar molecules (He)

Limitations of the Ideal Gas Law

High Pressure Limitations

- Ideal gas law assumes molecules have negligible volume and do not interact with each other which breaks down at high pressures
- At high pressures, the finite volume of molecules becomes significant relative to the container volume leading to lower molar volumes than predicted
- Repulsive intermolecular forces at high pressures cause the pressure to be higher than predicted by the ideal gas law
- The compressibility factor of real gases deviates significantly from unity ($Z > 1$) at high pressures indicating non-ideal behavior

Low Temperature Limitations

- At low temperatures, the attractive intermolecular forces between gas molecules become more significant causing deviations from ideal behavior
- Real gases have lower pressure and molar volume than predicted by the ideal gas law at low temperatures due to the increased influence of attractive forces
- The compressibility factor of real gases is typically less than unity ($Z < 1$) at low temperatures indicating non-ideal behavior
- As temperature decreases, real gases may condense into liquids or solids, a behavior not accounted for by the ideal gas law which assumes gases remain in the gaseous state at all temperatures

3.2 Virial equation of state

The virial equation of state expands on the ideal gas law, accounting for real gas behavior. It uses a power series with virial coefficients to describe how molecules interact at different pressures and temperatures.

Understanding the virial equation helps us grasp how gases deviate from ideal behavior. By looking at the coefficients, we can see how molecular interactions change with temperature and pressure, giving us a

more accurate picture of real gases.

Virial Expansion and Coefficients

Virial Expansion Overview

- Represents a power series expansion of the compressibility factor Z in terms of molar volume $\tilde{V}$ or pressure P
- Allows for the calculation of thermodynamic properties of real gases at moderate pressures and densities
- Coefficients in the expansion are called virial coefficients and depend on temperature and the specific gas
- Truncating the series after a certain number of terms provides an approximation of the equation of state

Virial Coefficients

- Second virial coefficient $B(T)$ represents the first correction to ideal gas behavior
- Accounts for interactions between pairs of molecules
- Positive values indicate repulsive interactions dominate ($Z > 1$) while negative values indicate attractive interactions dominate ($Z < 1$)
- Third virial coefficient $C(T)$ represents the next level of correction
- Accounts for interactions among three molecules simultaneously
- Typically has a smaller effect than the second virial coefficient except at high densities
- Higher order coefficients (fourth, fifth, etc.) exist but are often negligible under most conditions

Truncation Considerations

- Truncating the virial expansion after the second term (using only $B(T)$) yields the second virial equation of state
- Provides a reasonable approximation for many gases at low to moderate pressures
- Including the third virial coefficient $C(T)$ extends the applicable range to higher pressures and densities
- Truncation errors increase at higher pressures and densities where molecular interactions become more significant
- The number of terms needed for accurate results depends on the specific gas and the conditions of interest

Virial Equation Forms

Pressure Explicit Form

- Virial equation written as a series expansion in pressure P
- $Z = 1 + B'P + C'P^2 + D'P^3 + \dots$

- Coefficients B' , C' , D' , etc. are related to the virial coefficients $B(T)$, $C(T)$, $D(T)$, etc.
- Useful for describing gas behavior at low to moderate pressures
- Allows for direct calculation of compressibility factor Z from pressure P

Volume Explicit Form

- Virial equation written as a series expansion in inverse molar volume $1/\tilde{V}$
- $Z = 1 + B/\tilde{V} + C/\tilde{V}^2 + D/\tilde{V}^3 + \dots$
- Coefficients B , C , D , etc. are the virial coefficients $B(T)$, $C(T)$, $D(T)$, etc.
- Useful for describing gas behavior at low to moderate densities
- Allows for direct calculation of compressibility factor Z from molar volume $\tilde{V}$

Molecular Interactions and Temperature Effects

Molecular Interactions

- Virial coefficients are related to the intermolecular potential energy between molecules
- Second virial coefficient $B(T)$ depends on the pair potential energy $u(r)$ between two molecules
- Positive values of $B(T)$ indicate predominantly repulsive interactions (hard sphere-like)
- Negative values of $B(T)$ indicate predominantly attractive interactions (van der Waals-like)
- Third and higher virial coefficients depend on potential energies involving three or more molecules
- Represent multi-body interactions and are more complex to calculate

Temperature Dependence

- Virial coefficients are functions of temperature T
- Second virial coefficient $B(T)$ typically decreases with increasing temperature
- At high temperatures, kinetic energy dominates and molecular interactions become less significant
- At low temperatures, attractive interactions become more important and $B(T)$ becomes more negative
- Third and higher virial coefficients also vary with temperature but the dependence is often weaker than for $B(T)$
- The temperature dependence of virial coefficients reflects the changing balance between repulsive and attractive interactions as temperature changes

3.3 Cubic equations of state (van der Waals, Redlich-Kwong, Peng-Robinson)

Cubic equations of state improve on the ideal gas law by accounting for real gas behavior. They include the van der Waals, Redlich-Kwong, and Peng-Robinson equations, which consider molecular attraction and volume.

These equations use parameters based on critical properties and the acentric factor. They help predict fluid behavior across a wide range of conditions, especially near the critical point and in vapor-liquid equilibrium.

Cubic Equations of State

Van der Waals Equation

- Proposed by Johannes Diderik van der Waals in 1873 to improve upon the ideal gas law by accounting for the behavior of real gases
- Modifies the ideal gas law by introducing two parameters: a represents the attraction between molecules and b represents the volume occupied by the molecules
- The van der Waals equation is given by: $(P + \frac{a}{V_m^2})(V_m - b) = RT$
- Captures the behavior of real gases more accurately than the ideal gas law, especially at high pressures and low temperatures (near the critical point)

Redlich-Kwong and Peng-Robinson Equations

- The Redlich-Kwong equation, proposed in 1949, further improves upon the van der Waals equation by introducing temperature-dependent parameters
- The Redlich-Kwong equation is given by: $P = \frac{RT}{V_m - b} - \frac{a}{\sqrt{T}V_m(V_m + b)}$
- The Peng-Robinson equation, developed in 1976, is similar to the Redlich-Kwong equation but uses a different attractive term to better represent the behavior of hydrocarbons
- The Peng-Robinson equation is given by: $P = \frac{RT}{V_m - b} - \frac{a(T)}{V_m(V_m + b) + b(V_m - b)}$

Equation Parameters and Compressibility Factor

- The parameters a and b in cubic equations of state are specific to each substance and are determined from critical properties (critical temperature, critical pressure, and acentric factor)
- The acentric factor (ω) is a measure of the non-sphericity of molecules and affects the attractive term in the Peng-Robinson equation
- The compressibility factor (Z) is the ratio of the actual molar volume to the molar volume of an ideal gas at the same temperature and pressure: $Z = \frac{PV_m}{RT}$
- Cubic equations of state can be expressed in terms of the compressibility factor, which allows for easier comparison between different equations and substances

Equation Components

Attractive and Repulsive Terms

- Cubic equations of state consist of two main components: an attractive term and a repulsive term
- The attractive term accounts for the intermolecular forces (van der Waals forces) that cause molecules to attract each other, leading to a decrease in pressure
- The repulsive term represents the volume occupied by the molecules and the repulsive forces between them, which cause an increase in pressure

- The balance between the attractive and repulsive terms determines the overall behavior of the fluid

Acentric Factor and Critical Properties

- The acentric factor (ω) is a measure of the non-sphericity of molecules and is used to characterize the shape and polarity of molecules
- Substances with higher acentric factors (e.g., long-chain hydrocarbons) have stronger attractive forces and deviate more from ideal gas behavior
- Critical properties (critical temperature, critical pressure, and critical volume) are used to determine the parameters in cubic equations of state
- The critical point represents the conditions at which the liquid and vapor phases become indistinguishable, and the fluid exhibits unique properties (e.g., infinite compressibility)

Critical Behavior and Equilibrium

Critical Point and Phase Behavior

- The critical point is the highest temperature and pressure at which a substance can exist as a liquid and vapor in equilibrium
- At the critical point, the density and other properties of the liquid and vapor phases become identical, and the fluid exhibits enhanced mass and heat transfer properties
- Cubic equations of state can be used to predict the phase behavior of fluids near the critical point, including the formation of vapor-liquid equilibrium and the calculation of critical properties

Vapor-Liquid Equilibrium and Phase Diagrams

- Vapor-liquid equilibrium (VLE) refers to the condition where a liquid and its vapor are in equilibrium with each other, meaning that the rates of evaporation and condensation are equal
- Cubic equations of state can be used to construct phase diagrams, which show the regions of pressure and temperature where different phases (solid, liquid, and vapor) exist in equilibrium
- Phase diagrams are essential for understanding the behavior of fluids under various conditions and for designing processes that involve phase changes (e.g., distillation, refrigeration)
- The shape of the phase diagram and the location of the critical point depend on the specific substance and can be predicted using cubic equations of state (e.g., the Peng-Robinson equation for hydrocarbons)

3.4 Corresponding states principle

The corresponding states principle is a powerful tool in thermodynamics. It lets us predict how substances behave by comparing them to well-known reference materials. This simplifies complex calculations and helps us understand diverse substances' properties.

By using reduced properties and the acentric factor, we can apply this principle to a wide range of substances. This approach is super useful for estimating thermodynamic properties without needing tons of experimental data for every single substance out there.

Critical Properties and Reduced Properties

Understanding Critical Properties

- Critical properties represent the highest temperature and pressure at which the liquid and vapor phases of a substance can coexist in equilibrium
- Critical temperature (T_c) is the highest temperature at which a substance can exist as a liquid
- Critical pressure (P_c) is the highest pressure at which a substance can exist as a liquid
- Critical volume (V_c) is the volume occupied by one mole of a substance at its critical point
- Critical properties are unique to each substance and can be determined experimentally or estimated using empirical correlations (Joback method, Lydersen method)

Reduced Properties and Their Significance

- Reduced properties are dimensionless quantities obtained by dividing the actual property by its corresponding critical value
- Reduced temperature: $T_r = \frac{T}{T_c}$
- Reduced pressure: $P_r = \frac{P}{P_c}$
- Reduced volume: $V_r = \frac{V}{V_c}$
- Reduced properties allow for the comparison of different substances at corresponding states, which is the basis of the corresponding states principle
- Substances at the same reduced temperature and pressure exhibit similar behavior and have similar reduced properties (density, enthalpy, entropy)

Compressibility Factor and Its Relation to Reduced Properties

- Compressibility factor (Z) is a measure of the deviation of a gas from ideal gas behavior
- Defined as: $Z = \frac{PV}{nRT}$, where P is pressure, V is volume, n is the number of moles, R is the universal gas constant, and T is temperature
- For an ideal gas, $Z = 1$, while for real gases, Z deviates from unity depending on the reduced temperature and pressure
- Compressibility factor is a function of reduced temperature and pressure: $Z = f(T_r, P_r)$
- This relationship forms the basis for the generalized compressibility charts and corresponding states principle

Generalized Compressibility

Generalized Compressibility Chart

- A graphical representation of the compressibility factor (Z) as a function of reduced pressure (P_r) and reduced temperature (T_r)
- Allows for the estimation of Z for a substance at given reduced conditions without the need for experimental data

- The chart is divided into different regions corresponding to different states of the substance (gas, liquid, supercritical fluid)
- The chart is based on the principle of corresponding states, which states that substances at the same reduced conditions exhibit similar behavior
- Example: Estimating the compressibility factor of nitrogen at 100 K and 10 MPa using the generalized compressibility chart

Two-Parameter Corresponding States Principle

- The two-parameter corresponding states principle assumes that the compressibility factor (Z) is a function of only reduced temperature (T_r) and reduced pressure (P_r)
- Mathematically: $Z = f(T_r, P_r)$
- This principle allows for the prediction of thermodynamic properties of a substance using the properties of a reference substance at the same reduced conditions
- The reference substance is typically a simple molecule with well-known properties (argon, methane)
- The two-parameter corresponding states principle works well for simple, non-polar substances but may not be accurate for complex or polar substances

Three-Parameter Corresponding States Principle and Acentric Factor

- The three-parameter corresponding states principle introduces a third parameter, the acentric factor (ω), to account for the shape and polarity of molecules
- Acentric factor is a measure of the deviation of a molecule's vapor pressure curve from that of a simple spherical molecule (acentric factor = 0 for argon)
- Mathematically: $Z = f(T_r, P_r, \omega)$
- The introduction of the acentric factor improves the accuracy of the corresponding states principle for complex and polar substances
- Acentric factor can be determined experimentally or estimated using empirical correlations (Pitzer's correlation, Lee-Kesler correlation)
- Example: Comparing the acentric factors of n-butane ($\omega = 0.201$) and carbon dioxide ($\omega = 0.239$) to explain their different behaviors at the same reduced conditions

Generalized Correlations

Application of Generalized Correlations in Thermodynamics

- Generalized correlations are empirical equations that relate thermodynamic properties (enthalpy, entropy, fugacity) to reduced properties and acentric factor
- These correlations are based on the three-parameter corresponding states principle and are valid for a wide range of substances
- Generalized correlations allow for the estimation of thermodynamic properties without the need for extensive experimental data
- Examples of generalized correlations include:

- Lee-Kesler correlation for enthalpy and entropy
- Pitzer's correlation for fugacity coefficients
- Edminster's correlation for vapor-liquid equilibrium ratios
- Generalized correlations are particularly useful in process design and simulation, where accurate thermodynamic properties are required for a variety of substances at different conditions

Limitations and Accuracy of Generalized Correlations

- Generalized correlations are empirical and may not be accurate for all substances, particularly those with unique molecular structures or strong intermolecular interactions
- The accuracy of generalized correlations depends on the quality of the experimental data used to develop them and the range of conditions for which they were derived
- Generalized correlations may not be suitable for substances near their critical points or at extreme conditions (high pressure, low temperature)
- When using generalized correlations, it is essential to be aware of their limitations and to validate their predictions against experimental data when possible
- In some cases, more sophisticated equations of state (Peng-Robinson, SAFT) or molecular simulations may be necessary to obtain accurate thermodynamic properties

Unit 4 – The First Law of Thermodynamics

4.1 Energy, heat, and work

Energy, heat, and work are fundamental concepts in thermodynamics. They're the building blocks for understanding how energy moves and changes in systems. These ideas help us grasp the First Law of Thermodynamics, which is all about energy conservation.

Knowing these concepts is crucial for analyzing real-world processes. From engines to refrigerators, energy transfer shapes our world. Understanding how energy flows and changes form helps us design more efficient systems and solve complex engineering problems.

Energy Types and Conservation

Internal Energy and Its Components

- Internal energy (U) represents the total energy contained within a system
- Includes kinetic energy due to the motion of molecules
- Includes potential energy from intermolecular forces and chemical bonds
- Kinetic energy (KE) is the energy associated with the motion of an object or particles
- Depends on the mass and velocity of the object or particles ($KE = \frac{1}{2}mv^2$)
- Examples: a moving car, gas molecules in motion
- Potential energy (PE) is the stored energy an object possesses due to its position or configuration
- Includes gravitational potential energy, elastic potential energy, and chemical potential energy
- Examples: a stretched spring, a book on a shelf, chemical bonds in molecules

Conservation of Energy Principle

- Energy conservation states that energy cannot be created or destroyed, only converted from one form to another
- The total energy of an isolated system remains constant over time
- Changes in one form of energy must be balanced by changes in other forms
- Energy can be transferred between systems through heat, work, or other mechanisms
- Example: in a power plant, chemical energy in fuel is converted to thermal energy, then to mechanical energy in turbines, and finally to electrical energy

Heat and Work

Heat Transfer Mechanisms

- Heat (Q) is the transfer of thermal energy between systems due to a temperature difference

- Heat can be transferred through three main mechanisms:
- Conduction: heat transfer through direct contact between substances (e.g., a hot pan on a stove)
- Convection: heat transfer through the movement of fluids or gases (e.g., hot air rising)
- Radiation: heat transfer through electromagnetic waves (e.g., sunlight warming the Earth)
- The direction of heat transfer is always from a higher temperature to a lower temperature

Work and Its Relationship to Energy

- Work (W) is the energy transfer that occurs when a force acts on an object over a distance
- Mathematically, work is the product of force and displacement in the direction of the force ($W = F \cdot d$)
- Work can be done on a system (positive work) or by a system (negative work)
- Example: compressing a gas (positive work), a gas expanding and pushing a piston (negative work)
- Work is a path function, meaning it depends on the process or path taken from the initial to the final state
- The relationship between work and energy is described by the work-energy theorem:
- The net work done on an object equals the change in its kinetic energy ($W_{net} = \Delta KE$)

Thermodynamic Systems

Defining a Thermodynamic System

- A thermodynamic system is a specific portion of the universe chosen for analysis
- It can be a physical system, such as a gas in a cylinder, or a conceptual system, like a heat engine
- The system is separated from its surroundings by a well-defined boundary
- The boundary can be fixed (e.g., rigid container) or movable (e.g., piston)
- The boundary can be real (e.g., walls of a container) or imaginary (e.g., a selected volume in a larger system)
- The type of system depends on the nature of its boundary and the allowed energy and matter exchange:
- Open system: can exchange both matter and energy with its surroundings
- Closed system: can exchange energy but not matter with its surroundings
- Isolated system: cannot exchange either matter or energy with its surroundings

Interactions Between System and Surroundings

- The surroundings are everything outside the chosen thermodynamic system
- Interactions between the system and surroundings occur through the system boundary
- These interactions can involve the exchange of energy (heat or work) and/or matter
- The direction and magnitude of these interactions determine the changes in the system's properties

- Example: heat flowing into a system increases its internal energy, while work done by the system decreases its internal energy
- Understanding the system, surroundings, and their interactions is crucial for applying the laws of thermodynamics and analyzing thermodynamic processes

4.2 Conservation of energy and the first law

The first law of thermodynamics is all about energy conservation. It's the foundation for understanding how energy moves and changes in systems. This law helps us track energy as it flows in and out, whether through heat, work, or mass transfer.

We use energy balance equations to apply the first law to real-world situations. These equations let us analyze both closed systems, which don't exchange mass, and open systems, which do. Understanding these concepts is key to solving thermodynamic problems.

First Law and Energy Balance

Conservation of Energy

- First law of thermodynamics states energy cannot be created or destroyed, only converted from one form to another
- Energy balance is the accounting of energy transfer into and out of a system
- Based on the principle of conservation of energy
- Includes heat transfer, work, and changes in internal, kinetic, and potential energy
- Closed system does not exchange mass with its surroundings, only energy (heat and work)
- Examples include a sealed piston-cylinder device or a rigid, sealed tank
- Open system exchanges both mass and energy with its surroundings
- Also known as a control volume
- Examples include a turbine, nozzle, diffuser, or heat exchanger

Energy Balance Equations

- First law for a closed system: $\Delta E_{system} = Q - W$
- ΔE_{system} is the change in total energy of the system (internal, kinetic, and potential)
- Q is the net heat transfer into the system
- W is the net work done by the system
- Energy balance for an open system: $\Delta E_{CV} = Q - W + \sum \dot{m}_{in} (h + \frac{V^2}{2} + gz) - \sum \dot{m}_{out} (h + \frac{V^2}{2} + gz)$
- ΔE_{CV} is the change in total energy of the control volume
- $\dot{m}$ is the mass flow rate
- h is the specific enthalpy, $\frac{V^2}{2}$ is the specific kinetic energy, and gz is the specific potential energy

Thermodynamic Processes

Steady-State and Transient Processes

- Steady-state process occurs when a system operates under steady conditions and all properties are independent of time
- Examples include a power plant operating at constant load or a refrigerator maintaining a constant temperature
- Transient process occurs when a system undergoes changes in its properties with time
- Also known as an unsteady process
- Examples include startup or shutdown of a power plant, or a batch chemical reactor

Adiabatic and Isothermal Processes

- Adiabatic process occurs when there is no heat transfer between a system and its surroundings ($Q = 0$)
- Can be reversible (quasi-equilibrium) or irreversible
- Examples include a well-insulated piston-cylinder device or a rapid expansion or compression
- Isothermal process occurs at constant temperature
- Requires heat transfer between the system and surroundings to maintain constant temperature
- Examples include a piston-cylinder device with a heat reservoir, or a phase change process at constant pressure (boiling or condensation)

4.3 Enthalpy and specific heats

Enthalpy and specific heats are key concepts in thermodynamics. They help us understand how energy moves in systems and how materials respond to temperature changes. This knowledge is crucial for analyzing heat transfer and energy transformations.

The first law of thermodynamics deals with energy conservation. Enthalpy and specific heats are tools that let us quantify energy changes in various processes, connecting nicely to the broader themes of the chapter.

Enthalpy and Specific Heats

Definition and Calculation of Enthalpy

- Enthalpy represents the total heat content of a system
- Defined as the sum of the internal energy and the product of pressure and volume ($H = U + pV$)
- Enthalpy is a state function, meaning its value depends only on the current state of the system, not the path taken to reach that state
- Changes in enthalpy can be calculated using the specific heat capacity of a substance
- Specific heat capacity is the amount of heat required to raise the temperature of a unit mass of a substance by one degree (units: J/kg·K)

- The change in enthalpy (ΔH) is equal to the mass (m) times the specific heat capacity (C) times the change in temperature (ΔT): $\Delta H = mc\Delta T$

Constant Pressure and Constant Volume Specific Heats

- The specific heat capacity of a substance can vary depending on the conditions under which heat is added
- Constant pressure specific heat (C_p) is the amount of heat required to raise the temperature of a unit mass of a substance by one degree at constant pressure
- Constant volume specific heat (C_v) is the amount of heat required to raise the temperature of a unit mass of a substance by one degree at constant volume
- For an ideal gas, the constant pressure specific heat is always greater than the constant volume specific heat
- This is because at constant pressure, some of the added heat goes into doing work to expand the gas, while at constant volume, all of the added heat goes into increasing the internal energy (and thus temperature) of the gas
- The relationship between C_p and C_v for an ideal gas is given by $C_p - C_v = R$, where R is the specific gas constant

Heat Transfer

Sensible Heat

- Sensible heat refers to the heat that causes a change in temperature without a change in phase
- When sensible heat is added or removed from a substance, its temperature changes, but it remains in the same phase (solid, liquid, or gas)
- The amount of sensible heat transferred can be calculated using the specific heat capacity and the change in temperature ($Q = mc\Delta T$)
- Examples of sensible heat transfer include:
 - Heating water in a pot on a stove (temperature increases, but water remains liquid)
 - Cooling a metal object by immersing it in cold water (temperature decreases, but metal remains solid)

Latent Heat

- Latent heat is the heat absorbed or released by a substance during a phase change without a change in temperature
- When a substance undergoes a phase change (melting, vaporization, freezing, or condensation), it absorbs or releases heat while maintaining a constant temperature
- The amount of latent heat transferred depends on the mass of the substance and the specific latent heat for the phase change (fusion or vaporization)
- Examples of latent heat transfer include:
 - Melting ice to form liquid water (heat is absorbed, but temperature remains at 0°C until all ice has melted)

- Boiling water to form steam (heat is absorbed, but temperature remains at 100°C until all water has vaporized)

Thermodynamic Properties

Heat Capacity Ratio

- The heat capacity ratio (γ) is the ratio of the constant pressure specific heat to the constant volume specific heat: $\gamma = c_p/c_v$
- For an ideal gas, the heat capacity ratio is a constant that depends only on the number of degrees of freedom of the gas molecules
- Monatomic gases (e.g., helium) have a heat capacity ratio of 5/3, diatomic gases (e.g., nitrogen) have a heat capacity ratio of 7/5, and polyatomic gases have lower values
- The heat capacity ratio is an important parameter in many thermodynamic processes
- It appears in the equation for the speed of sound in a gas: $c = \sqrt{\gamma R_{specific} T}$, where $R_{specific}$ is the specific gas constant and T is the absolute temperature
- It also determines the relationship between pressure and volume during an adiabatic process (one with no heat transfer): $pV^\gamma = constant$

4.4 Applications to closed and open systems

The first law of thermodynamics is crucial for analyzing energy transfers in closed and open systems. It helps us understand how energy flows in various devices like nozzles, turbines, and heat exchangers. This knowledge is essential for designing efficient machines and processes.

Closed systems have fixed mass, while open systems allow mass flow. The steady flow energy equation is key for open systems, balancing energy inputs and outputs. We'll look at how these principles apply to real-world devices and processes.

Closed and Open Systems

System Analysis

- Closed system analysis examines a fixed mass that does not exchange matter with its surroundings
- Open system analysis involves a control volume that allows mass to cross its boundaries
- Control volume is a region in space chosen for thermodynamic analysis of mass flow (nozzles, diffusers, turbines)
- Mass flow rate ($\dot{m}$) represents the amount of mass flowing through a cross-sectional area per unit time

Conservation Principles

- Conservation of mass principle states that mass cannot be created or destroyed within a closed system
- For an open system, the net change in mass within the control volume equals mass flow in minus mass flow out

- Conservation of energy principle asserts that energy cannot be created or destroyed, only converted from one form to another
- Energy entering an open system (via heat, work, or mass flow) must equal the energy leaving plus the change in energy of the system

Steady Flow Devices

Steady Flow Energy Equation

- Steady flow energy equation (SFEE) applies the conservation of energy to a control volume at steady state
- Assumes no change in properties over time at any point within the control volume
- SFEE states that the rate of energy transfer into a steady flow system equals the rate of energy transfer out
- Includes energy transfer by heat, work, and mass flow
- Energy flow rate ($\dot{E}$) represents the amount of energy crossing the boundary of a control volume per unit time

Devices and Applications

- Nozzles and diffusers are steady flow devices that convert between kinetic and pressure energy
- Nozzles accelerate fluid flow and decrease pressure (rocket nozzles)
- Diffusers decelerate flow and increase pressure (wind tunnel diffusers)
- Turbines and compressors involve steady flow with work interactions
- Turbines extract work from a fluid as it expands and pressure decreases (steam turbines in power plants)
- Compressors input work to increase the pressure of a flowing fluid (jet engine compressors)

Other Devices and Processes

Throttling and Heat Exchange

- Throttling process involves a significant pressure drop without any work interaction (flow through a valve or porous plug)
- Occurs at constant enthalpy in the absence of heat transfer and work
- Commonly used to regulate pressure and flow rate in refrigeration and air conditioning systems
- Heat exchangers facilitate heat transfer between two flowing fluid streams without mixing them
- Employ a solid wall to separate the fluids and prevent mass exchange
- Widely used in applications like engine cooling, process heating, and air conditioning (radiators, shell-and-tube exchangers)

Transient and Non-Steady Processes

- Many real-world processes involve changes in properties over time and do not strictly adhere to the steady flow assumption
- Transient processes involve gradual changes in system properties (startup or shutdown of a power plant)
- Non-steady processes exhibit fluctuations or cyclic variations (internal combustion engines, reciprocating compressors)
- Analysis of transient and non-steady processes often employs quasi-equilibrium assumptions or averages properties over time
- Quasi-equilibrium assumes the process occurs slowly enough that properties are uniform at any instant
- Time-averaging techniques can provide a simplified steady-state approximation for cyclic processes

Unit 5 – The Second Law of Thermodynamics

5.1 Directionality of processes and thermal efficiency

The Second Law of Thermodynamics introduces entropy and directionality in processes. It states that isolated systems' entropy always increases, reaching a maximum at equilibrium. This law sets limits on heat engines and explains why heat flows from hot to cold.

Thermal efficiency measures how well heat engines convert heat to work. The Second Law caps efficiency, with the Carnot cycle as the theoretical max. Real engines always fall short due to irreversibilities, but understanding these limits helps improve practical designs.

Second Law of Thermodynamics

Fundamental Principles and Statements

- Second Law of Thermodynamics establishes the concept of entropy and the directionality of thermodynamic processes
- States that the total entropy of an isolated system always increases over time, approaching a maximum value at thermodynamic equilibrium
- Kelvin-Planck statement asserts that it is impossible to construct a device that operates in a cycle, produces no other effect than the removal of heat from a single reservoir, and the performance of an equivalent amount of work
- Implies that no heat engine can have a thermal efficiency of 100%
- Clausius statement declares that heat cannot spontaneously flow from a colder body to a hotter body without external work being performed
- Indicates the natural direction of heat transfer is from high temperature to low temperature regions

Spontaneous Processes and Entropy

- Spontaneous processes occur naturally without any external intervention or work input
- Examples include heat flow from hot to cold objects, gas expansion into a vacuum, and mixing of fluids
- Entropy is a measure of the disorder or randomness in a system
- Second Law states that the entropy of the universe always increases during spontaneous processes
- Provides a quantitative way to determine the directionality and feasibility of thermodynamic processes
- Reversible processes are idealized processes that can be reversed without any change in the system or surroundings
- Require infinitesimally small changes and occur in perfect equilibrium
- Serve as a theoretical limit for the maximum efficiency of real processes

Thermal Efficiency and Heat Engines

Thermal Efficiency and its Implications

- Thermal efficiency (η) is a measure of the effectiveness of a heat engine in converting heat input into useful work output
- Defined as the ratio of net work output (W_{net}) to heat input (Q_{in}): $\eta = \frac{W_{net}}{Q_{in}}$
- Second Law limits the maximum thermal efficiency achievable by any heat engine operating between two thermal reservoirs
- Carnot efficiency (η_{Carnot}) represents the theoretical upper limit: $\eta_{Carnot} = 1 - \frac{T_{cold}}{T_{hot}}$
- Where T_{cold} and T_{hot} are the absolute temperatures of the cold and hot reservoirs, respectively
- Practical heat engines (steam turbines, internal combustion engines) always have efficiencies lower than the Carnot efficiency due to irreversibilities and losses

Reversible and Irreversible Processes in Heat Engines

- Reversible processes in heat engines are idealized processes that occur infinitely slowly and maintain the system in thermal equilibrium at each step
- Involve no dissipative effects (friction, heat loss) and can be reversed without any net change in the system or surroundings
- Examples include isothermal expansion/compression and adiabatic expansion/compression in an ideal gas
- Irreversible processes are real processes that involve dissipative effects and cannot be reversed without changes in the system or surroundings
- Occur due to friction, heat transfer across finite temperature differences, and non-equilibrium conditions
- Examples include rapid expansion/compression, heat transfer through finite temperature gradients, and combustion processes
- Presence of irreversibilities reduces the thermal efficiency of practical heat engines compared to the ideal Carnot efficiency
- Minimizing irreversibilities (improved insulation, lubrication) can help increase the efficiency of real heat engines

5.2 Carnot cycle and thermodynamic temperature scale

The Carnot cycle is a key concept in thermodynamics, showing how heat engines work at their best. It's all about turning heat into work efficiently, using a series of steps that move heat between hot and cold places.

The thermodynamic temperature scale builds on the Carnot cycle idea. It gives us a way to measure temperature that doesn't depend on any specific material, starting from absolute zero where there's no heat at all.

Carnot Cycle and Efficiency

Carnot Cycle Concepts

- Carnot cycle represents the most efficient heat engine cycle operating between two thermal energy reservoirs at constant temperatures
- Consists of four reversible processes: isothermal expansion, adiabatic expansion, isothermal compression, and adiabatic compression
- Carnot cycle is an ideal thermodynamic cycle that provides an upper limit on the efficiency of any classical thermodynamic engine
- Operates in a closed system, meaning the working fluid is returned to its initial state at the end of each cycle (piston-cylinder device)

Carnot Engine Characteristics

- Carnot engine is a theoretical heat engine that operates on the Carnot cycle
- Consists of a heat source at a high temperature (T_H), a heat sink at a low temperature (T_L), and a working fluid (ideal gas)
- Work is done by the working fluid during the isothermal expansion process, while work is done on the working fluid during the isothermal compression process
- Carnot engines are the most efficient heat engines that operate between two specific temperatures

Ideal Gas Carnot Cycle Processes

- Isothermal expansion: gas expands at constant temperature T_H while in contact with the hot reservoir, absorbing heat and doing work ($pV = nRT$)
- Adiabatic expansion: gas continues to expand without exchanging heat with the surroundings, causing its temperature to decrease from T_H to T_L
- Isothermal compression: gas is compressed at constant temperature T_L while in contact with the cold reservoir, releasing heat and having work done on it
- Adiabatic compression: gas is further compressed without exchanging heat, causing its temperature to increase from T_L back to T_H

Carnot Efficiency Calculation

- Carnot efficiency (η_{Carnot}) represents the maximum efficiency attainable by a heat engine operating between two temperatures
- Defined as the ratio of the net work output (W) to the heat input from the hot reservoir (Q_H):
$$\eta_{Carnot} = \frac{W}{Q_H} = 1 - \frac{Q_L}{Q_H}$$
- For an ideal gas Carnot cycle, the efficiency can be expressed in terms of the reservoir temperatures:
$$\eta_{Carnot} = 1 - \frac{T_L}{T_H}$$
- Carnot efficiency increases as the temperature difference between the hot and cold reservoirs increases (steam power plants, internal combustion engines)

Thermodynamic Temperature Scale

Absolute Temperature and Absolute Zero

- Thermodynamic temperature scale is based on the concept of absolute zero, the lowest possible temperature
- Absolute zero is the temperature at which a system has no thermal energy and cannot transfer heat to any other system
- Kelvin (K) is the SI unit of thermodynamic temperature, with 0 K representing absolute zero (-273.15°C or -459.67°F)
- Temperatures on the Kelvin scale are always positive, as they represent the absolute magnitude of thermal energy

Relation to Reversible Heat Engines

- The thermodynamic temperature scale is defined by the efficiency of reversible heat engines, such as the Carnot engine
- For reversible heat engines, the ratio of heat transferred ($\frac{Q_H}{Q_L}$) is equal to the ratio of the absolute temperatures of the reservoirs ($\frac{T_H}{T_L}$)
- This relationship allows for the establishment of an absolute temperature scale that is independent of the properties of any particular substance (ideal gas law)

Practical Implications and Applications

- Thermodynamic temperature is essential for understanding and analyzing heat engine efficiency and performance
- Absolute zero is a fundamental limit in thermodynamics and cannot be reached in practice, as it would require an infinite number of steps in a Carnot cycle (third law of thermodynamics)
- Cryogenics and ultra-low temperature research aim to achieve temperatures as close to absolute zero as possible (superconductivity, quantum computing)
- The thermodynamic temperature scale is used in various fields, including physics, chemistry, and engineering, to describe the thermal behavior of systems (heat transfer, chemical reactions, materials science)

5.3 Clausius inequality and entropy

The Clausius inequality and entropy are key concepts in thermodynamics. They help us understand how energy flows and changes in systems. The Clausius inequality sets limits on heat transfer, while entropy measures disorder and energy availability.

These ideas are crucial for the Second Law of Thermodynamics. They explain why some processes happen naturally and others don't. Understanding entropy helps us analyze real-world systems and improve energy efficiency in machines and processes.

Clausius Inequality and Entropy

Defining Clausius Inequality

- States that cyclic integral of $\delta Q/T$ is always less than or equal to zero
- Applies to any thermodynamic cycle
- Helps determine the direction of heat transfer between a system and its surroundings
- Fundamental inequality in thermodynamics that leads to the concept of entropy

Introducing Entropy

- Measure of disorder or randomness in a system
- Quantifies the amount of energy that is unavailable for useful work
- Defined as $dS = \delta Q_{rev}/T$ where dS is the change in entropy, δQ_{rev} is the heat transferred reversibly, and T is the absolute temperature
- SI unit is joules per kelvin (J/K)

Entropy as a State Function

- Value depends only on the current state of the system, not on how it got there
- Change in entropy ΔS depends only on initial and final states
- Can be calculated using $\Delta S = \int_1^2 \frac{\delta Q_{rev}}{T}$ for a reversible process between states 1 and 2
- Enables determination of entropy change for any process, reversible or irreversible, by considering a hypothetical reversible path between the same initial and final states

Calculating Entropy Change

- For an internally reversible process, $\Delta S = \int_1^2 \frac{\delta Q}{T}$
- For an ideal gas undergoing a reversible process, $\Delta S = mc_v \ln \frac{T_2}{T_1} + mR \ln \frac{V_2}{V_1}$ where m is mass, c_v is specific heat at constant volume, R is gas constant, T is temperature, and V is volume
- For an incompressible substance undergoing a reversible process, $\Delta S = mc \ln \frac{T_2}{T_1}$ where c is specific heat
- Total entropy change of a system and its surroundings is always greater than or equal to zero for any real process

Second Law and Entropy Generation

Stating the Second Law in Terms of Entropy

- Total entropy of an isolated system always increases for irreversible processes and remains constant for reversible processes
- Mathematically expressed as $\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings} \geq 0$

- Provides a criterion for determining the direction of a process - one that increases total entropy is possible, while one that decreases total entropy is impossible
- Establishes entropy as a fundamental property that governs the behavior of thermodynamic systems

Understanding Entropy Generation

- Refers to the increase in total entropy due to irreversibilities within a system or process
- Caused by factors such as friction, unrestrained expansion, heat transfer through a finite temperature difference, mixing of dissimilar substances, and chemical reactions
- Quantified by the entropy generation term S_{gen} in the entropy balance equation

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings} = S_{gen} \geq 0$$
- Represents a measure of the lost potential for useful work in a system or process

Relating Irreversibility to Entropy Generation

- Irreversible processes always generate entropy, while reversible processes have zero entropy generation
- Degree of irreversibility is directly proportional to the amount of entropy generated
- Examples of irreversible processes include spontaneous heat transfer from hot to cold objects, unrestrained expansion of a gas, and friction in mechanical systems
- Reversible processes are idealized and can only be approached in real systems by minimizing irreversibilities

Isentropic Processes

Defining Isentropic Processes

- Processes in which entropy remains constant ($\Delta S = 0$)
- Occur when a system undergoes a reversible adiabatic process
- Commonly used as a model for rapid compression or expansion processes in devices such as pumps, turbines, and compressors
- Isentropic efficiency is a measure of how closely a real process approximates an isentropic process

Understanding Reversible Processes

- Processes that can be reversed without any net change in the system or its surroundings
- Occur infinitely slowly and involve no dissipative effects such as friction or unrestrained expansion
- Characterized by zero entropy generation ($S_{gen} = 0$)
- Serve as ideal limits against which real processes can be compared
- Examples include reversible isothermal expansion or compression of an ideal gas, reversible heat transfer between two reservoirs at infinitesimally different temperatures

Exploring Adiabatic Processes

- Processes in which no heat is transferred between the system and its surroundings ($Q = 0$)
- Can be reversible (isentropic) or irreversible
- For an ideal gas undergoing a reversible adiabatic process, $PV^\gamma = \text{constant}$ where γ is the specific heat ratio
- Adiabatic processes are rapid compared to heat transfer timescales, making them good approximations for many real-world processes
- Examples include rapid compression in diesel engines, expansion in gas turbines, and propagation of sound waves in gases

5.4 Entropy changes in reversible and irreversible processes

Entropy changes in processes are crucial for understanding the Second Law of Thermodynamics. They show how energy quality degrades in real-world systems, distinguishing between ideal reversible processes and practical irreversible ones.

T-s diagrams and isentropic efficiency help visualize and quantify these changes. The entropy balance and principle of increase guide our understanding of energy flow and system behavior in thermodynamic processes.

Entropy Changes in Processes

Reversible Processes and Entropy Change

- In a reversible process, the system and surroundings can be restored to their initial states without any net change in the universe
- The entropy change of a system during a reversible process is calculated by integrating dQ/T over the process path
- For a reversible isothermal process, the entropy change is given by $\Delta S = Q/T$, where Q is the heat transfer and T is the constant temperature
- In a reversible adiabatic process (isentropic process), the entropy change is zero since there is no heat transfer ($Q = 0$)

Irreversible Processes and Entropy Change

- Irreversible processes result in a net increase in the entropy of the universe due to friction, unrestrained expansion, heat transfer through a finite temperature difference, or mixing of two different substances
- The entropy change for an irreversible process is always greater than that for a reversible process between the same two end states
- For an irreversible adiabatic process, the entropy of the system increases, while for an irreversible isothermal process, both the system and surroundings experience an increase in entropy

T-s Diagrams and Isentropic Efficiency

- T-s (Temperature-Entropy) diagrams are useful for visualizing and analyzing processes in terms of entropy changes
- The area under a reversible process curve on a T-s diagram represents the heat transfer during that process
- Isentropic efficiency is a measure of the deviation of an actual process from the corresponding isentropic process between the same end states
- For a compression process, the isentropic efficiency is defined as the ratio of the work input required for the isentropic process to the actual work input ($\eta_c = w_s/w_a$)
- For an expansion process, it is the ratio of the actual work output to the isentropic work output ($\eta_t = w_a/w_s$)

Entropy Balance and Principle

Entropy Balance

- The entropy balance is a statement of the second law of thermodynamics, expressing the change in entropy of a system in terms of the entropy transfer and entropy generation
- For a closed system, the entropy change (ΔS) is the sum of the entropy transfer by heat (Q/T) and the entropy generated within the system due to irreversibilities (S_{gen})
- In an open system, entropy can also be transferred by mass flow across the system boundaries
- The entropy balance for an open system is given by $dS/dt = \sum(Q/T) + \sum m_{in}S_{in} - \sum m_{out}S_{out} + S_{gen}$, where m is the mass flow rate and S is the specific entropy

Principle of Increase of Entropy

- The principle of increase of entropy states that the entropy of an isolated system always increases for irreversible processes and remains constant for reversible processes
- In any real process, the entropy generation term is always positive due to irreversibilities, leading to an increase in the entropy of the universe
- This principle places constraints on the direction of heat transfer and the spontaneity of processes, as natural processes occur in the direction of increasing entropy
- The second law of thermodynamics can be stated in terms of entropy: the entropy of the universe always increases in real processes

Applications of Entropy

Heat Engines and Entropy

- Heat engines operate between a high-temperature reservoir (source) and a low-temperature reservoir (sink), converting some of the heat input into useful work
- The thermal efficiency of a heat engine is limited by the Carnot efficiency, which depends on the ratio of the absolute temperatures of the reservoirs

- The entropy change of the universe for a heat engine cycle is zero for a reversible cycle and positive for an irreversible cycle
- In a Carnot cycle, the entropy change of the system is zero, and the entropy changes of the hot and cold reservoirs are equal and opposite ($Q_H/T_H = Q_L/T_L$)

Refrigerators, Heat Pumps, and Entropy

- Refrigerators and heat pumps are devices that transfer heat from a low-temperature region to a high-temperature region by consuming work
- The coefficient of performance (COP) of a refrigerator or heat pump is the ratio of the desired heat transfer to the work input
- The maximum COP for a refrigerator ($Q_L/(Q_H - Q_L)$) and a heat pump ($Q_H/(Q_H - Q_L)$) is achieved by a reversible Carnot cycle operating between the same temperature limits
- In an irreversible refrigeration cycle or heat pump cycle, the entropy generation is positive, resulting in a lower COP compared to the reversible case

Unit 6 – Entropy and the Third Law of Thermodynamics

6.1 Absolute entropy and the third law

Absolute entropy and the Third Law are key concepts in thermodynamics. They help us understand how energy behaves in systems at extremely low temperatures. This knowledge is crucial for predicting material properties and designing efficient processes.

The Third Law states that perfect crystals have zero entropy at absolute zero. This gives us a starting point to calculate entropy at any temperature. Understanding absolute entropy helps us grasp energy distribution and availability in systems.

Absolute Entropy and the Third Law

The Third Law and Absolute Entropy

- States the entropy of a perfect crystalline substance at absolute zero temperature is zero
- Provides a reference point for determining absolute entropy values
- Allows for the calculation of absolute entropy at any temperature by integrating the heat capacity from absolute zero to the desired temperature
- Absolute entropy quantifies the degree of disorder or randomness in a system
- Measured in units of joules per kelvin (J/K)
- Represents the amount of energy dispersed within a system that is unavailable for useful work

Nernst Heat Theorem and Entropy at Absolute Zero

- The Nernst heat theorem states that as a system approaches absolute zero, the change in entropy for any process approaches zero
- Implies that the entropy of a perfect crystal at absolute zero is zero
- Provides a theoretical basis for the Third Law of Thermodynamics
- At absolute zero (0 K or -273.15°C), the entropy of a perfect crystal is zero
- All atoms in the crystal are in their lowest energy state and have no thermal motion
- There is no disorder or randomness in the system at this temperature

Perfect Crystals and Zero-Point Entropy

Characteristics of Perfect Crystals

- A perfect crystal is a theoretical construct in which the atoms are arranged in a perfect lattice structure
- Each atom occupies a specific position in the lattice
- There are no defects, impurities, or thermal vibrations in the crystal

- In reality, perfect crystals do not exist due to the presence of imperfections and thermal motion at finite temperatures
- Real crystals have defects (vacancies, interstitials, dislocations) and impurities that contribute to entropy

Zero-Point Entropy and Its Implications

- Zero-point entropy refers to the residual entropy that exists in some systems even at absolute zero
- Occurs when there are multiple equivalent ground states or configurations with the same lowest energy
- Examples include certain alloys, glasses, and polymers with frozen-in disorder
- The presence of zero-point entropy indicates that the Third Law of Thermodynamics is not strictly followed in these systems
- The entropy does not reach zero at absolute zero temperature
- Highlights the limitations of the Third Law and the concept of perfect crystals

Exceptions to the Third Law

Residual Entropy and Its Causes

- Residual entropy is the entropy that remains in a system at absolute zero temperature
- Arises from the presence of multiple equivalent ground states or configurations
- Occurs in systems with frozen-in disorder, such as certain alloys (Cu-Au alloys), glasses (silica glass), and polymers (rubber)
- The existence of residual entropy challenges the strict interpretation of the Third Law
- Suggests that the entropy of these systems does not reach zero at absolute zero
- Indicates that the Third Law is an idealization that applies to perfect crystals but not all real systems

Examples and Implications of Residual Entropy

- Ice (H₂O) has residual entropy due to the random orientation of hydrogen bonds in its crystal structure
- Even at absolute zero, there are multiple equivalent configurations of hydrogen bonds
- Leads to a non-zero entropy value at 0 K, estimated to be around 3.4 J/K per mole of water
- The presence of residual entropy has practical implications in materials science and engineering
- Affects the stability, mechanical properties, and thermal behavior of materials
- Needs to be considered when designing and characterizing materials for low-temperature applications

6.2 Calculation of entropy changes

Calculating entropy changes is crucial for understanding thermodynamic processes. This topic explores how to quantify entropy changes in various scenarios, from reversible to irreversible processes, using mathematical formulas and concepts like the Clausius inequality.

The section covers entropy changes under specific conditions, such as isothermal, isobaric, isochoric, and adiabatic processes. It also introduces temperature-entropy diagrams as a visual tool for analyzing thermodynamic systems and their entropy changes.

Entropy Changes in Different Processes

Calculating Entropy Change

- Entropy change quantifies the change in disorder or randomness of a system during a process
- Calculated using the integral $\Delta S = \int \frac{dQ_{rev}}{T}$, where dQ_{rev} is the reversible heat transfer and T is the absolute temperature
- Entropy is a state function, meaning the change in entropy depends only on the initial and final states, not the path taken between them
- SI unit for entropy is joules per kelvin (J/K)

Reversible and Irreversible Processes

- Reversible processes occur infinitely slowly, allowing the system to remain in equilibrium with its surroundings at all times
- Examples include isothermal expansion of an ideal gas, melting of ice at its melting point
- Irreversible processes occur rapidly, causing the system to deviate from equilibrium with its surroundings
- Examples include spontaneous heat transfer from hot to cold objects, expansion of a gas into a vacuum
- Entropy change for a reversible process is given by $\Delta S = \int \frac{dQ_{rev}}{T}$, while for an irreversible process, it is $\Delta S > \int \frac{dQ}{T}$

Clausius Inequality

- The Clausius inequality states that for any cyclic process, the integral of $\frac{dQ}{T}$ is always less than or equal to zero: $\oint \frac{dQ}{T} \leq 0$
- For a reversible cyclic process, the equality holds: $\oint \frac{dQ_{rev}}{T} = 0$
- The Clausius inequality demonstrates that the entropy of an isolated system never decreases, consistent with the second law of thermodynamics

Entropy Changes Under Specific Conditions

Isothermal and Isobaric Processes

- Isothermal entropy change occurs when a system undergoes a process at constant temperature
- For an ideal gas, the isothermal entropy change is given by $\Delta S = nR \ln \frac{V_2}{V_1}$, where n is the number of moles, R is the gas constant, and V_1 and V_2 are the initial and final volumes
- Isobaric entropy change occurs when a system undergoes a process at constant pressure

- For an ideal gas, the isobaric entropy change is given by $\Delta S = nC_p \ln \frac{T_2}{T_1}$, where C_p is the molar heat capacity at constant pressure and T_1 and T_2 are the initial and final temperatures

Isochoric and Adiabatic Processes

- Isochoric entropy change occurs when a system undergoes a process at constant volume
- For an ideal gas, the isochoric entropy change is given by $\Delta S = nC_v \ln \frac{T_2}{T_1}$, where C_v is the molar heat capacity at constant volume
- Adiabatic entropy change occurs when a system undergoes a process with no heat transfer to or from the surroundings
- For an adiabatic process, the entropy change is always zero: $\Delta S = 0$
- Examples include adiabatic compression or expansion of a gas in an insulated cylinder

Graphical Representation

Temperature-Entropy (T-s) Diagram

- A T-s diagram is a graphical representation of a thermodynamic process, with temperature on the y-axis and entropy on the x-axis
- Isothermal processes appear as horizontal lines on a T-s diagram, as temperature remains constant
- Isobaric processes have a positive slope on a T-s diagram, as both temperature and entropy increase
- Isochoric processes have a positive slope on a T-s diagram, similar to isobaric processes
- Adiabatic processes appear as vertical lines on a T-s diagram, as entropy remains constant with no heat transfer
- The area under the curve on a T-s diagram represents the heat transfer during the process:

$$Q = \int TdS$$

6.3 Maxwell relations and thermodynamic manipulations

Maxwell relations are powerful tools that link different thermodynamic properties. They're derived from the equality of mixed partial derivatives of thermodynamic potentials, allowing us to calculate hard-to-measure properties from easier ones.

Thermodynamic potentials, like Gibbs and Helmholtz free energies, help us understand system behavior at equilibrium. These functions, along with enthalpy and internal energy, characterize a system's state and predict its tendency to change.

Maxwell Relations and Thermodynamic Potentials

Maxwell Relations

- Derived from equality of mixed second partial derivatives of thermodynamic potentials
- Relate changes in thermodynamic properties to each other
- Four key Maxwell relations:
- $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$

- $(\frac{\partial T}{\partial P})_S = (\frac{\partial V}{\partial S})_P$
- $(\frac{\partial S}{\partial V})_T = (\frac{\partial P}{\partial T})_V$
- $(\frac{\partial S}{\partial P})_T = -(\frac{\partial V}{\partial T})_P$

• Enable calculation of hard-to-measure properties from easier-to-measure ones (entropy from pressure-volume data)

Thermodynamic Potentials

- State functions that characterize thermodynamic systems at equilibrium
- Gibbs free energy (G)
 - Measures maximum reversible work obtainable from a system at constant temperature and pressure
 - Defined as $G = H - TS$, where H is enthalpy, T is temperature, and S is entropy
 - Minimized at equilibrium for systems at constant temperature and pressure (chemical reactions, phase transitions)
- Helmholtz free energy (A)
 - Measures maximum reversible work obtainable from a system at constant temperature and volume
 - Defined as $A = U - TS$, where U is internal energy
 - Minimized at equilibrium for systems at constant temperature and volume (elastic deformations)
- Enthalpy (H)
 - Measures heat content of a system at constant pressure
 - Defined as $H = U + PV$, where P is pressure and V is volume
 - Changes in enthalpy equal heat absorbed or released at constant pressure (calorimetry)
- Internal energy (U)
 - Total kinetic and potential energy of a system's particles
 - Changes in internal energy equal heat absorbed or work done on the system (first law of thermodynamics)

Mathematical Tools for Thermodynamics

Partial Derivatives and Jacobian Matrix

- Partial derivatives measure rates of change of a function with respect to one variable while holding others constant
- Jacobian matrix organizes partial derivatives of a vector-valued function
- Enables coordinate transformations and change of variables in thermodynamic equations
- Example: Jacobian determinant relates $(\frac{\partial P}{\partial V})_T$ to $(\frac{\partial V}{\partial P})_T$ via $(\frac{\partial P}{\partial V})_T = \frac{1}{(\frac{\partial V}{\partial P})_T}$
- Partial derivatives and Jacobians essential for manipulating thermodynamic equations and applying Maxwell relations

Thermodynamic Equations of State

- Relate thermodynamic properties of a system at equilibrium
- Ideal gas law: $PV = nRT$, where n is number of moles and R is the gas constant
- Describes behavior of gases at low densities and high temperatures
- Van der Waals equation: $(P + \frac{an^2}{V^2})(V - nb) = nRT$, where a and b are constants specific to the gas
- Accounts for molecular size and intermolecular attractions, improving upon ideal gas law
- Virial equation: $\frac{PV}{nRT} = 1 + \frac{B(T)}{V} + \frac{C(T)}{V^2} + \dots$, where $B(T)$, $C(T)$, etc. are virial coefficients dependent on temperature
- Expresses compressibility factor as a power series in reciprocal molar volume
- Useful for describing real gas behavior at moderate densities
- Equations of state combined with Maxwell relations and thermodynamic potentials enable complete characterization of thermodynamic systems

6.4 Entropy generation and exergy

Entropy generation and exergy are key concepts in thermodynamics. They help us understand how energy quality degrades in real processes. This affects the efficiency of engines, power plants, and other systems we use every day.

By studying entropy generation and exergy, we can figure out where energy is being wasted. This knowledge lets engineers design better, more efficient machines that use less fuel and create less pollution.

Entropy Generation and Irreversibility

Entropy Generation and Its Implications

- Entropy generation refers to the increase in entropy of a system and its surroundings during a process
- Occurs due to irreversibilities such as friction, heat transfer through a finite temperature difference, mixing of fluids, and inelastic deformation
- Leads to a decrease in the available energy for useful work and an increase in the disorder or randomness of the system
- Has important implications for the efficiency and sustainability of energy systems (power plants, engines, refrigerators)

Irreversibility and Its Consequences

- Irreversibility is a measure of the deviation of a process from an ideal, reversible process
- Arises from dissipative effects such as friction, heat transfer, and mixing that generate entropy
- Causes a loss of useful work potential and a reduction in the efficiency of energy conversion processes

- Cannot be eliminated completely in real-world systems but can be minimized through careful design and optimization (insulation, lubrication, streamlining)

Exergy Destruction and Its Significance

- Exergy destruction represents the loss of available work due to irreversibilities in a process
- Quantifies the degradation of energy quality and the reduction in the ability to perform useful work
- Occurs whenever entropy is generated, as dictated by the Gouy-Stodola theorem ($\dot{X}_{destroyed} = T_0 \dot{S}_{gen}$)
- Provides a measure of the thermodynamic inefficiency of a system and identifies the sources of irreversibility (heat exchangers, turbines, compressors)
- Minimizing exergy destruction is crucial for improving the performance and sustainability of energy systems (cogeneration, waste heat recovery)

Exergy and Available Work

Exergy: A Measure of Energy Quality

- Exergy is the maximum useful work that can be obtained from a system as it reaches equilibrium with a specified reference environment (dead state)
- Represents the quality or potential of energy to cause change and perform work
- Depends on both the state of the system and the reference environment (temperature, pressure, chemical composition)
- Can be divided into different forms such as physical exergy (due to temperature and pressure differences), chemical exergy (due to composition differences), and kinetic and potential exergy
- Is consumed or destroyed during irreversible processes, leading to a reduction in the available work (heat transfer, combustion, mixing)

Available Work and Its Calculation

- Available work is the maximum useful work that can be obtained from a system in a given state as it undergoes a reversible process to the dead state
- Represents the exergy of the system relative to the reference environment
- Can be calculated using the exergy balance equation, considering the exergy of the system, the exergy of heat and work interactions, and the exergy destruction ($\dot{X}_{in} - \dot{X}_{out} - \dot{X}_{destroyed} = \Delta \dot{X}_{system}$)
- Is always less than the total energy of the system due to irreversibilities and the constraints imposed by the second law of thermodynamics
- Maximizing available work is a key objective in the design and optimization of energy systems (power plants, engines, heat pumps)

Reversible Work and Its Significance

- Reversible work is the maximum useful work that can be obtained from a system undergoing a reversible process between two specified states

- Represents the upper limit of work output or the minimum work input required for a process
- Is achieved when the process occurs infinitely slowly, with no dissipative effects or irreversibilities (friction, heat transfer, mixing)
- Serves as a benchmark for evaluating the performance of real processes and identifying the potential for improvement
- Can be calculated using the exergy balance equation, setting the exergy destruction term to zero ($\dot{X}_{in} - \dot{X}_{out} = \Delta X_{system}$)

Dead State and Its Role in Exergy Analysis

- The dead state is the reference environment with which a system is assumed to be in equilibrium at the end of a process
- Typically defined by specifying the temperature, pressure, and chemical composition of the surroundings (ambient conditions, standard atmosphere)
- Represents the state of zero exergy, where the system has no potential to perform useful work
- Serves as the basis for calculating the exergy of a system and evaluating its available work potential
- Can vary depending on the location and the specific application, affecting the results of exergy analysis (altitude, climate, resource availability)

Second Law Analysis

Second Law Efficiency and Its Application

- Second law efficiency, also known as exergetic efficiency, is a measure of the thermodynamic performance of a system or process
- Defined as the ratio of the actual useful work output to the maximum possible (reversible) work output, or the ratio of the minimum work input to the actual work input
- Accounts for both the quantity and quality of energy, considering the irreversibilities and exergy destruction in the system
- Provides a more meaningful and comprehensive assessment of efficiency compared to first law efficiency, which only considers energy conservation
- Can be applied to various energy systems and processes, including power plants, engines, refrigerators, and heat exchangers, to identify inefficiencies and potential improvements

Exergy Balance and Its Components

- The exergy balance is a statement of the conservation of exergy for a system or control volume, accounting for the exergy flows, exergy destruction, and exergy accumulation
- Consists of three main components: exergy of the system, exergy of heat and work interactions, and exergy destruction
- Exergy of the system represents the available work potential associated with the state of the system relative to the reference environment

- Exergy of heat and work interactions accounts for the exergy associated with energy transfers across the system boundary (heat transfer, shaft work, electrical work)
- Exergy destruction represents the loss of available work due to irreversibilities within the system, as quantified by the Gouy-Stodola theorem
- Can be applied to steady-state or transient processes, with the exergy accumulation term included for transient analysis ($\dot{X}_{in} - \dot{X}_{out} - \dot{X}_{destroyed} = \frac{dX_{system}}{dt}$)
- Provides a framework for analyzing the performance, identifying the sources of inefficiency, and optimizing the design of energy systems (power plants, engines, heat exchangers)

Unit 7 – Fluid Thermodynamic Properties

7.1 Fundamental property relations

Thermodynamic property relations are the backbone of fluid behavior analysis. They connect state variables like pressure and temperature to energy functions like enthalpy and Gibbs free energy, helping us predict how fluids will react under different conditions.

These fundamental relations are crucial for understanding fluid systems. By linking measurable properties to abstract concepts like entropy, we can solve real-world engineering problems and design more efficient processes in industries from power generation to chemical manufacturing.

Thermodynamic State Variables

Internal Energy, Enthalpy, and Entropy

- Internal energy represents the total energy of a thermodynamic system, including kinetic and potential energy of particles, as well as intermolecular forces
- Enthalpy is a state function that measures the total heat content of a system at constant pressure, defined as $H = U + PV$
- Entropy is a measure of the disorder or randomness of a system, representing the amount of energy unavailable for useful work (second law of thermodynamics)

Pressure, Volume, and Temperature

- Pressure is the force per unit area exerted by a fluid on its surroundings, measured in pascals (Pa) or atmospheres (atm)
- Volume is the amount of space occupied by a substance, typically measured in cubic meters (m^3) or liters (L)
- Temperature is a measure of the average kinetic energy of particles in a system, expressed in Kelvin (K) or degrees Celsius ($^{\circ}C$)

Thermodynamic Potentials

Gibbs and Helmholtz Free Energy

- Gibbs free energy is a thermodynamic potential that measures the maximum reversible work that can be performed by a system at constant temperature and pressure, defined as $G = H - TS$
- Helmholtz free energy is a thermodynamic potential that measures the maximum reversible work that can be performed by a system at constant temperature and volume, defined as $A = U - TS$
- Both Gibbs and Helmholtz free energy are useful in determining the spontaneity and equilibrium conditions of chemical reactions and phase transitions

Thermodynamic Potentials and Their Relationships

- Thermodynamic potentials are state functions that describe the energy content and work potential of a system under specific constraints (constant temperature, pressure, volume, or entropy)

- The four primary thermodynamic potentials are internal energy (U), enthalpy (H), Gibbs free energy (G), and Helmholtz free energy (A)
- These potentials are related to each other through Legendre transformations, which involve expressing one potential in terms of another by adding or subtracting the product of an intensive and extensive variable (e.g., $H = U + PV$)

Fundamental Property Relations

Maxwell Relations

- Maxwell relations are a set of four equations that describe the relationships between partial derivatives of thermodynamic potentials with respect to their natural variables
- These relations are derived from the equality of mixed second partial derivatives of thermodynamic potentials (e.g., $(\partial S/\partial P)_T = -(\partial V/\partial T)_P$)
- Maxwell relations are useful in determining hard-to-measure properties from more easily measured ones, such as calculating the change in entropy from measurements of volume and temperature

Partial Derivatives and Their Applications

- Partial derivatives are used to describe how a thermodynamic property changes with respect to one variable while holding other variables constant
- Common partial derivatives in thermodynamics include $(\partial P/\partial V)_T$ (isothermal compressibility), $(\partial V/\partial T)_P$ (isobaric thermal expansion), and $(\partial S/\partial T)_V$ (isochoric heat capacity)
- Partial derivatives are essential for deriving equations of state, such as the ideal gas law ($PV = nRT$), and for understanding the behavior of materials under different conditions (e.g., phase transitions, thermal expansion, and compressibility)

7.2 Residual properties

Residual properties are crucial for understanding real gas behavior. They measure how actual gases deviate from ideal gas models, helping engineers predict and analyze real-world systems more accurately.

Fugacity and compressibility factor are key concepts in this topic. They provide practical tools for calculating properties of real gases, essential for designing and optimizing processes in industries like chemical engineering and HVAC.

Residual Properties

Relationship between Residual Properties and Ideal Gas State

- Residual properties quantify the deviation of a real gas from the behavior of an ideal gas at the same temperature and pressure
- Calculated by subtracting the property value for an ideal gas from the actual property value of the real gas
- Ideal gas state serves as a reference point for comparing the behavior of real gases
- In an ideal gas, molecules have no intermolecular forces and occupy negligible volume

- Real gases deviate from ideal gas behavior due to intermolecular interactions and finite molecular volume

Residual Gibbs Free Energy, Enthalpy, and Entropy

- Residual Gibbs free energy (G^R) represents the difference between the actual Gibbs free energy of a real gas and that of an ideal gas at the same temperature and pressure
- Quantifies the non-ideality of a gas in terms of Gibbs free energy
- Positive G^R indicates a higher Gibbs free energy than an ideal gas, while negative G^R indicates a lower Gibbs free energy
- Residual enthalpy (H^R) is the difference between the actual enthalpy of a real gas and that of an ideal gas at the same temperature and pressure
- Measures the additional enthalpy due to intermolecular interactions in a real gas
- Positive H^R indicates higher enthalpy than an ideal gas, while negative H^R indicates lower enthalpy
- Residual entropy (S^R) represents the difference between the actual entropy of a real gas and that of an ideal gas at the same temperature and pressure
- Quantifies the entropy change associated with the non-ideality of a gas
- Negative S^R indicates a lower entropy than an ideal gas, while positive S^R indicates a higher entropy (less common)

Departure Functions and Their Applications

- Departure functions express the difference between the actual property value of a real gas and that of an ideal gas at the same temperature and pressure
- Denoted by the superscript "D" (e.g., G^D , H^D , S^D)
- Related to residual properties: $G^D = G^R$, $H^D = H^R$, $S^D = S^R$
- Departure functions are useful for estimating the properties of real gases when direct experimental data is unavailable
- Can be calculated using equations of state (EOS) or generalized correlations
- Example: Peng-Robinson EOS can be used to calculate departure functions for hydrocarbons and their mixtures
- Departure functions find applications in process design, equipment sizing, and thermodynamic analysis of real gas systems
- Example: Calculating the required compressor power for a natural gas pipeline considering the non-ideal behavior of the gas

Fugacity and Compressibility

Fugacity and Fugacity Coefficient

- Fugacity (f) is a thermodynamic property that represents the effective pressure of a real gas, accounting for its non-ideal behavior

- Has units of pressure (e.g., Pa, bar)
- For an ideal gas, fugacity equals the actual pressure
- For a real gas, fugacity can be higher or lower than the actual pressure, depending on the gas and the conditions
- Fugacity coefficient (ϕ) is the ratio of a gas's fugacity to its actual pressure at a given temperature and pressure
- Dimensionless quantity
- For an ideal gas, $\phi = 1$
- For a real gas, ϕ can be greater than or less than 1, indicating positive or negative deviations from ideal behavior
- Fugacity and fugacity coefficient are related by: $f = \phi P$
- P is the actual pressure of the gas
- Fugacity coefficient can be calculated using equations of state or experimentally measured

Compressibility Factor and Its Relation to Fugacity

- Compressibility factor (Z) is the ratio of the actual volume of a gas to the volume it would occupy if it behaved as an ideal gas at the same temperature and pressure
- Dimensionless quantity
- For an ideal gas, $Z = 1$
- For a real gas, Z can be greater than or less than 1, indicating positive or negative deviations from ideal behavior
- Compressibility factor is related to the fugacity coefficient by: $\ln \phi = \int_0^P \frac{Z-1}{P} dP$
- This relationship allows the calculation of fugacity coefficient from compressibility factor data
- Example: Using the virial equation of state to express Z as a function of pressure and calculating ϕ by integration
- Compressibility factor is used to characterize the behavior of real gases and to estimate their properties
- Can be obtained from experimental data (e.g., PVT measurements) or calculated using equations of state
- Generalized compressibility factor charts (e.g., Nelson-Obert charts) provide Z values for various gases as a function of reduced temperature and pressure

7.3 Generalized correlations for gases and liquids

Generalized correlations help predict fluid behavior across various conditions. They use reduced properties and the principle of corresponding states to compare different substances. These tools are crucial for understanding how gases and liquids deviate from ideal behavior.

The compressibility factor and virial equation of state are key concepts in these correlations. They account for real gas behavior and intermolecular forces, allowing engineers to make accurate predictions about

fluid properties in diverse applications.

Corresponding States and Reduced Properties

Principle of Corresponding States and Reduced Properties

- Corresponding states principle suggests that fluids at the same reduced state have similar deviation from ideal gas behavior
- Reduced properties are obtained by normalizing thermodynamic properties (temperature, pressure, volume) with respect to critical point values
- Reduced temperature: $T_R = T/T_c$
- Reduced pressure: $P_R = P/P_c$
- Reduced volume: $V_R = V/V_c$
- Critical properties (temperature T_c , pressure P_c , volume V_c) characterize the critical point, where liquid and vapor phases become indistinguishable

Acentric Factor and Fluid Behavior

- Acentric factor ω is a measure of the deviation of a fluid's behavior from that of a simple fluid (spherical molecules)
- Simple fluids (argon, krypton) have $\omega \approx 0$
- Complex fluids (hydrocarbons, refrigerants) have higher values of ω
- Acentric factor is defined as: $\omega = -\log_{10}(P_R^{sat}) - 1$ at $T_R = 0.7$, where P_R^{sat} is the reduced vapor pressure
- Incorporating acentric factor improves the accuracy of corresponding states correlations for a wide range of fluids

Generalized Compressibility Charts

Compressibility Factor and Charts

- Compressibility factor Z relates the actual behavior of a gas to that of an ideal gas: $Z = \frac{PV}{nRT}$
- For an ideal gas, $Z = 1$
- Deviations from ideality result in $Z \neq 1$
- Generalized compressibility charts (Nelson-Obert, Brown) plot Z as a function of reduced temperature and pressure
- Different charts are used for different values of acentric factor

Lee-Kesler and Pitzer Correlations

- Lee-Kesler correlation is a widely used corresponding states method for estimating compressibility factor and other properties
- Based on a three-parameter corresponding states principle (reduced temperature, reduced pressure, acentric factor)

- Provides accurate results for a wide range of fluids and conditions
- Pitzer correlations are another set of corresponding states correlations for estimating fluid properties
- Pitzer's two-parameter corresponding states principle uses reduced temperature and pressure
- Pitzer's three-parameter corresponding states principle adds the acentric factor for improved accuracy

Virial Equation of State

Virial Equation and Compressibility Factor

- Virial equation of state is a power series expansion that relates pressure to molar volume and temperature: $Z = 1 + \frac{B(T)}{V_m} + \frac{C(T)}{V_m^2} + \dots$
- $B(T)$ is the second virial coefficient, $C(T)$ is the third virial coefficient, and so on
- Virial coefficients depend on temperature and account for intermolecular interactions
- Truncating the virial equation after the second term yields: $Z = 1 + \frac{B(T)}{V_m}$
- Suitable for low-density gases
- Second virial coefficient can be estimated using Pitzer-type correlations or Tsonopoulos correlation
- Virial equation provides a more accurate description of gas behavior compared to the ideal gas equation, especially at higher pressures

7.4 Thermodynamic charts and their applications

Thermodynamic charts are visual tools that help us understand how fluids behave under different conditions. They show relationships between properties like pressure, temperature, and entropy, making it easier to analyze and solve complex problems.

These charts are crucial for engineers and scientists working with fluids. By using them, we can quickly see how changes in one property affect others, helping us design more efficient systems and make better decisions in real-world applications.

Thermodynamic Diagrams

Mollier Diagram and Temperature-Entropy (T-s) Diagram

- Mollier diagram plots enthalpy (h) on the vertical axis and entropy (s) on the horizontal axis
- Used to analyze thermodynamic processes and cycles involving steam or other working fluids
- Temperature-entropy (T-s) diagram plots temperature on the vertical axis and entropy on the horizontal axis
- Useful for analyzing ideal gas processes and cycles
- Constant pressure lines are typically shown as near-vertical lines
- Constant volume lines are typically shown as near-horizontal lines
- Both diagrams allow for easy visualization of thermodynamic processes such as isothermal (constant temperature), isobaric (constant pressure), and isentropic (constant entropy) processes

Pressure-Enthalpy (P-h) Diagram and Psychrometric Chart

- Pressure-enthalpy (P-h) diagram plots pressure on the vertical axis and enthalpy on the horizontal axis
- Commonly used for analyzing refrigeration cycles and heat pump systems
- Saturated liquid and saturated vapor lines form a dome-shaped region on the diagram
- Constant temperature lines are typically shown as near-horizontal lines within the saturated region
- Psychrometric chart is a graphical representation of the thermodynamic properties of moist air
- Plots various properties such as dry-bulb temperature, wet-bulb temperature, relative humidity, and specific humidity
- Used in the analysis and design of air-conditioning systems and other processes involving moist air
- Processes such as heating, cooling, humidification, and dehumidification can be easily visualized on the chart

Compressibility Factor Charts

Compressibility Factor and Its Applications

- Compressibility factor (Z) is a measure of the deviation of a real gas from ideal gas behavior
- Defined as the ratio of the actual volume of a gas to the volume it would occupy if it were an ideal gas at the same temperature and pressure
- $Z = 1$ for an ideal gas, and $Z \neq 1$ for a real gas
- Compressibility factor charts, also known as Z -charts, plot the compressibility factor as a function of reduced pressure and reduced temperature
- Reduced pressure (P_r) is the ratio of the actual pressure to the critical pressure of the gas
- Reduced temperature (T_r) is the ratio of the actual temperature to the critical temperature of the gas
- Z -charts are used to determine the compressibility factor of a real gas at given conditions, which is essential for accurate calculations involving real gas properties and processes

Generalized Enthalpy and Entropy Departure Charts

- Generalized enthalpy departure charts plot the difference between the actual enthalpy of a real gas and the enthalpy of an ideal gas (enthalpy departure) as a function of reduced pressure and reduced temperature
- Used to determine the actual enthalpy of a real gas at given conditions
- Enthalpy departure is typically expressed as $(h - h_{\text{ideal}}) / RT_c$, where R is the gas constant and T_c is the critical temperature
- Generalized entropy departure charts plot the difference between the actual entropy of a real gas and the entropy of an ideal gas (entropy departure) as a function of reduced pressure and reduced temperature
- Used to determine the actual entropy of a real gas at given conditions

- Entropy departure is typically expressed as $(s - s_{\text{ideal}}) / R$, where R is the gas constant
- Both enthalpy and entropy departure charts are essential tools for analyzing thermodynamic processes and cycles involving real gases, as they account for the non-ideal behavior of gases at high pressures and low temperatures

Unit 8 – Phase Equilibria and Stability

8.1 Criteria for phase equilibrium

Phase equilibrium is crucial for understanding how substances behave under different conditions. It's all about balance - when different phases of a material can coexist without changing. This happens when the chemical potentials of each component are equal across all phases.

Knowing these criteria helps predict phase transitions, like boiling or freezing. It's super useful for designing processes in chemical engineering, understanding geological phenomena, and even cooking! The key is minimizing Gibbs free energy to find the most stable state.

Equilibrium Fundamentals

Types of Equilibrium

- Thermal equilibrium occurs when two systems have reached the same temperature and there is no net heat transfer between them
- Achieved through thermal contact and exchange of energy until thermal motion of particles equalizes (conduction, convection, radiation)
- Example: A hot metal object placed in a room will eventually cool down to room temperature
- Mechanical equilibrium is reached when there is no net force acting on a system and no tendency for movement or deformation
- Balanced forces such as pressure, tension, and gravity result in a stable, static configuration
- Example: A book resting on a table experiences equal and opposite forces from gravity and the table's normal force
- Chemical equilibrium is attained when the forward and reverse rates of a chemical reaction are equal, resulting in no net change in concentrations over time
- Occurs in closed systems where reactants and products coexist at constant amounts determined by the equilibrium constant
- Example: The reversible reaction of hydrogen and iodine gas to form hydrogen iodide reaches equilibrium when the rates of formation and decomposition are balanced
- Equilibrium conditions are the specific constraints that must be satisfied for a system to be in overall thermodynamic equilibrium
- Requires simultaneous thermal, mechanical, and chemical equilibrium
- Characterized by uniform temperature, pressure, and chemical potential throughout the system
- Represents the most stable state with no tendency for spontaneous change

Achieving Equilibrium

- Equilibrium is reached through the spontaneous processes of energy and mass transfer that minimize differences in intensive properties
- Systems naturally evolve towards equilibrium to maximize entropy and minimize free energy

- Non-equilibrium states have gradients or imbalances that drive net flows until uniformity is achieved
- The approach to equilibrium is gradual and asymptotic, with the rate of change decreasing as the system gets closer to the final balanced state
- Equilibration timescales depend on factors like system size, material properties, and mixing mechanisms
- Example: Adding a drop of dye to water results in initial concentration gradients that slowly dissipate through diffusion until the color is evenly distributed
- Isolated systems always progress towards equilibrium, while open systems may be maintained in steady-state non-equilibrium conditions by external inputs and outputs
- Equilibrium represents a dynamic balance with ongoing microscopic fluctuations but no net macroscopic changes
- Living organisms are examples of open systems that constantly exchange energy and matter with their surroundings to sustain ordered structures and processes

Thermodynamic Criteria

Gibbs Free Energy Minimization

- The equilibrium state of a system is the one that minimizes the total Gibbs free energy (G) at constant temperature and pressure
- Gibbs free energy represents the maximum reversible work that can be extracted from a system
- Spontaneous processes always proceed in the direction of decreasing G until the minimum is reached at equilibrium
- For a pure substance, equilibrium corresponds to the lowest chemical potential (μ) among all possible phases at the given conditions
- Chemical potential measures the change in G with respect to the amount of substance added or removed
- Example: Water at atmospheric pressure exists as solid ice below 0°C, liquid water between 0-100°C, and water vapor above 100°C, each being the stable phase with minimum μ in its respective temperature range
- In multicomponent systems, equilibrium is determined by minimizing the total G while conserving the amounts of each component
- The equilibrium composition is calculated by solving a system of equations involving chemical potentials and mass balances
- Example: The distribution of a solute between two immiscible liquid phases (like iodine between water and carbon tetrachloride) reaches equilibrium when the chemical potentials in both phases are equal

Equality of Chemical Potentials

- At equilibrium, the chemical potential of each component must be uniform throughout the system and across all phases
- Chemical potential represents the energetic driving force for mass transfer and reaction

- Differences in chemical potential between phases or locations lead to spontaneous processes that restore equality
- For multiple phases in equilibrium, the chemical potentials of each component are equal in all phases
- This condition allows the calculation of partition coefficients, solubilities, and vapor pressures
- Example: The solubility of a gas in a liquid is determined by equating the chemical potential expressions for the gas and dissolved phases
- In reacting systems, equilibrium is reached when the sum of chemical potentials of reactants equals that of products, weighted by stoichiometric coefficients
- This relationship is equivalent to the minimization of Gibbs free energy and gives rise to the equilibrium constant expression
- Example: For the synthesis of ammonia from nitrogen and hydrogen ($N_2 + 3H_2 \rightleftharpoons 2NH_3$), equilibrium occurs when $\mu_{N_2} + 3\mu_{H_2} = 2\mu_{NH_3}$

Phase Coexistence

- At specific conditions of temperature and pressure, multiple phases of a substance can coexist in equilibrium
- Coexistence occurs along lines or curves in phase diagrams where the chemical potentials of the phases are equal
- Example: On the melting curve of a pure substance, solid and liquid phases have the same chemical potential and can exist together
- Phase transitions happen when the equilibrium shifts from one phase to another due to changes in conditions
- Transitions are characterized by abrupt changes in properties like density, enthalpy, and entropy
- Example: Boiling of a liquid occurs at the saturation temperature where the liquid and vapor chemical potentials become equal, resulting in a transition to the vapor phase
- The Gibbs Phase Rule ($F = C - P + 2$) relates the number of components (C), phases (P), and degrees of freedom (F) in a system at equilibrium
- Degrees of freedom represent the number of intensive variables that can be independently varied without changing the number of phases
- Example: For a single-component system with two phases in equilibrium (like water and steam), there is only one degree of freedom, so specifying either temperature or pressure automatically fixes the other variable along the coexistence curve

8.2 Chemical potential and Gibbs energy

Chemical potential and Gibbs energy are key concepts in thermodynamics. They help us understand how substances behave in mixtures and during phase changes. These ideas are crucial for predicting equilibrium conditions and spontaneous processes in various systems.

In this section, we'll explore how chemical potential relates to partial molar quantities and Gibbs energy. We'll also dive into the Gibbs-Duhem equation, equilibrium constants, and the Clausius-Clapeyron equation. These tools are essential for analyzing real-world thermodynamic problems.

Chemical Potential and Partial Molar Quantities

Definition and Significance of Chemical Potential

- Chemical potential (μ) represents the change in Gibbs free energy of a system when a component is added or removed while keeping temperature, pressure, and other component amounts constant
- Serves as a driving force for mass transfer and phase transitions in multicomponent systems
- Helps determine the direction of spontaneous processes and equilibrium conditions
- Plays a crucial role in understanding phase equilibria, chemical reactions, and transport phenomena

Partial Molar Quantities and Their Relationship to Chemical Potential

- Partial molar quantities describe the contribution of each component to the total thermodynamic property of a mixture
- Partial molar volume ($\bar{V}_i$) represents the change in total volume of a mixture when one mole of component i is added at constant temperature, pressure, and amounts of other components
- Partial molar enthalpy ($\bar{H}_i$) and partial molar entropy ($\bar{S}_i$) are defined similarly for enthalpy and entropy, respectively
- Chemical potential is related to partial molar quantities through the relationship $\mu_i = \bar{G}_i = \bar{H}_i - T\bar{S}_i + P\bar{V}_i$, where $\bar{G}_i$ is the partial molar Gibbs free energy

Gibbs-Duhem Equation and Its Applications

- Gibbs-Duhem equation relates changes in intensive properties (temperature, pressure, and chemical potentials) of a system at equilibrium
- For a multicomponent system, the equation is given by $SdT - VdP + \sum_i n_i d\mu_i = 0$, where S is entropy, V is volume, n_i is the number of moles of component i , and μ_i is the chemical potential of component i
- Provides a constraint on the changes in chemical potentials of components in a mixture
- Useful in deriving relationships between thermodynamic properties and determining the number of independent variables in a system
- Helps in the calculation of activity coefficients and fugacity coefficients in non-ideal mixtures (excess properties)

Gibbs Free Energy and Equilibrium

Gibbs Free Energy and Its Relation to Equilibrium

- Gibbs free energy (G) is a thermodynamic potential that measures the maximum reversible work that can be performed by a system at constant temperature and pressure
- Defined as $G = H - TS$, where H is enthalpy, T is temperature, and S is entropy
- Systems tend to minimize their Gibbs free energy to achieve equilibrium

- At equilibrium, the Gibbs free energy of a system is at its minimum, and the change in Gibbs free energy (dG) is zero
- For a closed system at constant temperature and pressure, the condition for equilibrium is $dG = 0$

Equilibrium Constant and Its Relationship to Gibbs Free Energy

- Equilibrium constant (K) is a measure of the position of equilibrium in a chemical reaction
- Relates the concentrations or partial pressures of reactants and products at equilibrium
- For a general reaction $aA + bB \rightleftharpoons cC + dD$, the equilibrium constant is given by $K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$, where $[X]$ represents the concentration or partial pressure of species X
- Gibbs free energy change of a reaction (ΔG) is related to the equilibrium constant through the equation $\Delta G = -RT \ln K$, where R is the universal gas constant and T is the absolute temperature
- This relationship allows the determination of the direction of a reaction and the calculation of equilibrium compositions

Clausius-Clapeyron Equation and Phase Equilibrium

- Clausius-Clapeyron equation describes the relationship between the vapor pressure of a substance and temperature at phase equilibrium
- For a phase transition (e.g., liquid-vapor), the equation is given by $\frac{dP}{dT} = \frac{\Delta H_{vap}}{T\Delta V}$, where P is the vapor pressure, T is the absolute temperature, ΔH_{vap} is the enthalpy of vaporization, and ΔV is the change in volume during the phase transition
- Helps in understanding the effect of temperature on vapor pressure and boiling point
- Useful in the design of distillation columns, heat exchangers, and other equipment involving phase changes
- Can be integrated to obtain the vapor pressure as a function of temperature, assuming ΔH_{vap} is constant (e.g., $\ln \frac{P_2}{P_1} = -\frac{\Delta H_{vap}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$)

Fugacity and Activity

Fugacity and Its Role in Non-Ideal Systems

- Fugacity (f) is a thermodynamic property that represents the effective partial pressure of a component in a non-ideal mixture
- Introduced to account for the deviations from ideal behavior in real systems
- For an ideal gas, fugacity is equal to the partial pressure ($f_i = P_i$)
- Fugacity coefficient (ϕ_i) is defined as the ratio of fugacity to partial pressure, $\phi_i = \frac{f_i}{P_i}$
- In non-ideal systems, fugacity is related to the chemical potential through the equation $\mu_i - \mu_i^0 = RT \ln \frac{f_i}{f_i^0}$, where μ_i^0 and f_i^0 are the chemical potential and fugacity at a reference state, respectively

Activity and Activity Coefficient

- Activity (a_i) is a measure of the effective concentration of a component in a non-ideal mixture
- Defined as the ratio of fugacity to a reference fugacity, $a_i = \frac{f_i}{f_i^0}$, where f_i^0 is the fugacity at a reference state (usually pure component at the same temperature and pressure)
- Activity coefficient (γ_i) is the ratio of activity to mole fraction, $\gamma_i = \frac{a_i}{X_i}$, where X_i is the mole fraction of component i
- For an ideal solution, activity coefficients are equal to unity ($\gamma_i = 1$)
- Activity coefficients account for the non-ideality of mixtures and are used in the calculation of phase equilibria, chemical reaction equilibria, and other thermodynamic properties
- Various models and equations, such as Margules, van Laar, and Wilson equations, are used to estimate activity coefficients based on experimental data or molecular interactions

8.3 Phase rule and Gibbs phase rule

Phase equilibria is all about balance. The Gibbs phase rule helps us understand how many variables we can change without messing up that balance. It's like a recipe for predicting what state matter will be in under different conditions.

Phase diagrams are like maps of matter's different states. They show us where solids, liquids, and gases hang out based on temperature and pressure. Special points on these maps, like the triple point, are where things get really interesting.

Gibbs Phase Rule

Degrees of Freedom and Variance

- Gibbs phase rule determines the degrees of freedom in a system at equilibrium
- Degrees of freedom represent the number of intensive variables (temperature, pressure, composition) that can be changed independently without affecting the number of phases in equilibrium
- Variance is another term for degrees of freedom
- A system with zero degrees of freedom (invariant) has a fixed equilibrium state and cannot be changed without changing the number of phases
- A system with one degree of freedom (univariant) can have one variable (temperature or pressure) changed without changing the number of phases
- A system with two degrees of freedom (bivariant) can have two variables changed independently without affecting the number of phases

Components and Phases

- Number of components (C) represents the minimum number of chemically independent species required to describe the composition of all phases in the system
- For a pure substance (water), $C = 1$
- For a binary solution (salt water), $C = 2$

- Number of phases (P) represents the number of physically distinct and mechanically separable regions in the system at equilibrium
- Examples of phases include solid, liquid, gas, or different solid phases (allotropes)
- Gibbs phase rule is expressed as $F = C - P + 2$, where F is the degrees of freedom (variance)
- The number 2 represents the two intensive variables (temperature and pressure) that can be varied independently

Phase Diagrams

Interpreting Phase Diagrams

- Phase diagram is a graphical representation of the equilibrium states of a substance under different conditions of temperature, pressure, and composition
- Regions on the phase diagram represent the stability ranges of different phases (solid, liquid, gas)
- Lines on the phase diagram represent the coexistence of two phases in equilibrium
- Solid-liquid coexistence line is called the melting or freezing curve
- Liquid-gas coexistence line is called the vaporization or condensation curve
- Solid-gas coexistence line is called the sublimation or deposition curve
- Points on the coexistence lines represent the equilibrium temperature and pressure for the two phases at a given composition

Special Points on Phase Diagrams

- Triple point is the unique temperature and pressure at which three phases (solid, liquid, and gas) coexist in equilibrium
- For water, the triple point occurs at 273.16 K (0.01°C) and 611.73 Pa
- Critical point is the temperature and pressure above which the distinction between liquid and gas phases disappears
- At the critical point, the properties of the liquid and gas phases become identical
- For water, the critical point occurs at 647.10 K (373.95°C) and 22.06 MPa
- Phase changes occur along the coexistence lines, while crossing the lines results in a change in the number and types of phases present at equilibrium
- For example, heating a solid at constant pressure above the melting point will result in a complete transformation to the liquid phase

8.4 Stability analysis and spinodal decomposition

Phase equilibria and stability are crucial in understanding material behavior. This section explores stability analysis and spinodal decomposition, key concepts in predicting phase transitions and separations.

We'll dive into thermodynamic stability, metastability, and the critical point. Then, we'll examine spinodal decomposition, nucleation, and the differences between binodal and spinodal curves in phase diagrams.

Thermodynamic Stability and Metastability

Stability and Metastability Concepts

- Thermodynamic stability refers to the state of a system at the global minimum of its Gibbs free energy
- Metastability is a state of a system that is locally stable but not globally stable
- Metastable states correspond to local minima in the Gibbs free energy landscape
- Examples of metastable states include supercooled liquids and supersaturated solutions
- The curvature of the Gibbs free energy determines the stability of a system
- Positive curvature indicates stability, while negative curvature indicates instability
- The inflection point between positive and negative curvature is the spinodal point

Critical Point and Stability

- The critical point is the point on a phase diagram where the properties of two phases become indistinguishable
- At the critical point, the distinction between liquid and gas phases disappears (critical opalescence)
- The critical point is characterized by a single value of temperature, pressure, and density
- The behavior of a system near the critical point is crucial for understanding phase transitions and stability
- Fluctuations in density and composition become significant near the critical point
- The critical point marks the boundary between stable and unstable regions on the phase diagram

Spinodal Decomposition and Phase Separation

Spinodal Decomposition Process

- Spinodal decomposition is a mechanism of phase separation that occurs in unstable regions of a phase diagram
- It involves the spontaneous separation of a system into two distinct phases without an energy barrier
- Spinodal decomposition is driven by the system's tendency to minimize its Gibbs free energy
- During spinodal decomposition, small fluctuations in composition grow over time, leading to the formation of interconnected domains
- The domains coarsen and eventually form two separate phases with different compositions
- Examples of spinodal decomposition include the separation of oil and water mixtures and the formation of microstructures in alloys

Nucleation and Phase Separation

- Nucleation is another mechanism of phase separation that occurs in metastable regions of a phase diagram

- It involves the formation of small clusters (nuclei) of a new phase within the existing phase
- Nucleation requires overcoming an energy barrier associated with the creation of an interface between the two phases
- The spinodal curve on a phase diagram separates the unstable region (where spinodal decomposition occurs) from the metastable region (where nucleation occurs)
- Inside the spinodal curve, the system is unstable, and phase separation occurs spontaneously
- Outside the spinodal curve but inside the binodal curve, the system is metastable, and phase separation occurs via nucleation

Binodal and Spinodal Curves

Binodal Curve Characteristics

- The binodal curve, also known as the coexistence curve, represents the boundary between the single-phase and two-phase regions on a phase diagram
- Points on the binodal curve correspond to equilibrium compositions of two coexisting phases
- The binodal curve is typically determined experimentally by measuring the compositions of coexisting phases at different temperatures
- The region inside the binodal curve is called the miscibility gap, where the system separates into two distinct phases
- The tie lines within the miscibility gap connect the compositions of the coexisting phases at a given temperature

Spinodal Curve and Critical Point

- The spinodal curve lies inside the binodal curve and represents the boundary between the metastable and unstable regions
- Points on the spinodal curve have a Gibbs free energy curvature of zero (inflection points)
- The spinodal curve is difficult to determine experimentally and is often calculated theoretically using thermodynamic models
- The binodal and spinodal curves meet at the critical point, where the distinction between the two curves disappears
- At the critical point, the two phases become indistinguishable, and the system exhibits critical phenomena (critical opalescence, diverging fluctuations)
- The shape of the binodal and spinodal curves near the critical point is important for understanding the behavior of systems undergoing phase transitions

Unit 9 – Fugacity and Activity in Thermodynamics

9.1 Concept of fugacity and fugacity coefficient

Fugacity is a key concept in thermodynamics, helping us understand how real gases behave differently from ideal ones. It measures a gas's tendency to escape and is used to apply ideal gas equations to real gases.

The fugacity coefficient shows how much a real gas deviates from ideal behavior. It's the ratio of fugacity to pressure and varies with temperature and pressure. Understanding fugacity helps us predict real gas behavior in various conditions.

Fugacity and Fugacity Coefficient

Fugacity as a Measure of Non-Ideality

- Fugacity measures the deviation of a real gas from ideal gas behavior
- Quantifies the "escaping tendency" or chemical potential of a real gas at a given temperature and pressure
- Has units of pressure (Pa, atm, bar) and approaches the pressure value as the gas approaches ideal behavior
- Allows for the application of ideal gas equations to real gases by replacing pressure with fugacity

Fugacity Coefficient and Its Relation to Pressure

- Fugacity coefficient (ϕ) is the ratio of fugacity to pressure (f/P) at a given temperature and pressure
- Represents the deviation of a real gas from ideal gas behavior
- For an ideal gas, $\phi = 1$ at all temperatures and pressures since $f = P$
- For a real gas, ϕ varies with temperature and pressure, typically decreasing with increasing pressure due to intermolecular interactions (van der Waals forces)
- Calculating fugacity coefficient requires an equation of state (EOS) such as van der Waals, Redlich-Kwong, or Peng-Robinson EOS

Gibbs Free Energy and Chemical Potential

Gibbs Free Energy as a Thermodynamic Potential

- Gibbs free energy (G) is a thermodynamic potential that measures the maximum reversible work that can be performed by a system at constant temperature and pressure
- Defined as $G = H - TS$, where H is enthalpy, T is temperature, and S is entropy
- Represents the balance between enthalpy (energy content) and entropy (disorder) in a system

- At equilibrium, the Gibbs free energy of a system is minimized ($dG = 0$) for spontaneous processes at constant temperature and pressure

Chemical Potential and Its Relation to Fugacity

- Chemical potential (μ) is the partial molar Gibbs free energy of a component in a mixture
- Represents the change in Gibbs free energy when one mole of a component is added to a system at constant temperature, pressure, and composition
- Related to fugacity by $\mu_i = \mu_i^0 + RT \ln(f_i/f_i^0)$, where μ_i^0 and f_i^0 are the chemical potential and fugacity at a reference state, and R is the universal gas constant
- At thermodynamic equilibrium, the chemical potentials of each component are equal in all phases ($\mu_i^\alpha = \mu_i^\beta = \mu_i^\gamma$)

Pressure Correction Factor

Pressure Correction Factor for Real Gases

- Pressure correction factor (Z) is the ratio of the actual volume of a real gas to the volume predicted by the ideal gas law at the same temperature and pressure
- Defined as $Z = \frac{PV}{nRT}$, where P is pressure, V is volume, n is the number of moles, R is the universal gas constant, and T is temperature
- Quantifies the deviation of a real gas from ideal gas behavior due to intermolecular interactions and finite molecular volume
- For an ideal gas, $Z = 1$ at all temperatures and pressures since $PV = nRT$

Calculating Pressure Correction Factor

- Pressure correction factor can be calculated using an equation of state (EOS) such as van der Waals, Redlich-Kwong, or Peng-Robinson EOS
- These EOS account for the non-ideality of real gases by introducing parameters that represent intermolecular attraction and repulsion forces, as well as the finite volume occupied by gas molecules
- Example: The van der Waals EOS is given by $(P + \frac{an^2}{V^2})(V - nb) = nRT$, where a and b are constants specific to the gas, representing intermolecular attraction and molecular volume, respectively
- Solving the EOS for Z yields a cubic equation in terms of the compressibility factor, which can be solved numerically or graphically (compressibility chart) to determine the pressure correction factor at a given temperature and pressure

9.2 Calculation methods for fugacity

Fugacity is a key concept in thermodynamics, helping us understand real gas behavior. It's like pressure, but accounts for non-ideal interactions between molecules. Knowing how to calculate fugacity is crucial for predicting phase equilibria and chemical reactions in real systems.

There are several ways to calculate fugacity, each with its pros and cons. From equations of state to graphical methods and generalized correlations, these techniques help us bridge the gap between ideal gas models and real-world behavior.

Equation of State Methods

Virial Equation and Compressibility Factor

- Equation of state method calculates fugacity using an equation that relates pressure, volume, and temperature of a substance
- Equations of state (ideal gas law, van der Waals equation, Redlich-Kwong equation) describe the behavior of gases and liquids under various conditions
- Virial equation is a power series expansion used to calculate the compressibility factor and fugacity of a gas
- Virial coefficients (B , C , D , etc.) depend on temperature and account for gas non-ideality due to intermolecular interactions
- Truncated after the second (B) or third (C) virial coefficient for most applications
- Compressibility factor (Z) measures the deviation of a gas from ideal behavior
- Defined as the ratio of the actual molar volume to the molar volume of an ideal gas at the same temperature and pressure
- $Z = 1$ for an ideal gas, $Z < 1$ for a gas with attractive intermolecular forces, and $Z > 1$ for a gas with repulsive intermolecular forces
- Calculated using the virial equation or equations of state (Redlich-Kwong, Peng-Robinson)

Graphical and Correlation Methods

Graphical Integration and Corresponding States Principle

- Graphical integration involves plotting experimental data (pressure vs. molar volume) and integrating the area under the curve to determine fugacity
- Requires accurate experimental data and numerical integration techniques (trapezoidal rule, Simpson's rule)
- Provides a visual representation of the relationship between pressure and molar volume
- Corresponding states principle states that substances at the same reduced temperature, pressure, and volume have similar properties
- Reduced properties are normalized by their critical values (reduced temperature $T_r = T/T_c$, reduced pressure $P_r = P/P_c$, reduced volume $V_r = V/V_c$)
- Allows for the prediction of properties for substances with limited experimental data using data from well-characterized substances (methane, carbon dioxide)

Generalized Correlations for Fugacity Calculation

- Generalized correlations are empirical equations that relate fugacity to reduced temperature, pressure, and volume
- Developed using experimental data for a wide range of substances
- Examples include the Lee-Kesler correlation and the Pitzer correlation

- Generalized correlations provide a quick and convenient method for estimating fugacity without the need for extensive experimental data or complex equations of state
- Require only the critical properties and acentric factor of the substance
- Less accurate than equations of state or graphical methods, particularly for substances with unique intermolecular interactions (hydrogen bonding, polar molecules)

Fugacity Calculation Rules

Lewis and Randall Rule for Ideal Mixtures

- Lewis and Randall rule states that the fugacity of a component in an ideal mixture is equal to its mole fraction multiplied by its fugacity in the pure state at the same temperature and pressure
- $\hat{f}_i = x_i f_i^0$, where $\hat{f}_i$ is the fugacity of component i in the mixture, x_i is the mole fraction of component i , and f_i^0 is the fugacity of pure component i at the same temperature and pressure
- Ideal mixtures are characterized by zero enthalpy of mixing, zero volume change on mixing, and no intermolecular interactions between unlike molecules
- Examples of ideal mixtures include mixtures of isotopes (helium-3 and helium-4) and mixtures of chemically similar substances (benzene and toluene)
- Lewis and Randall rule simplifies fugacity calculations for ideal mixtures by relating the mixture fugacity to pure component fugacities and mole fractions
- Requires knowledge of pure component fugacities, which can be calculated using equations of state, graphical methods, or generalized correlations
- Not applicable to non-ideal mixtures, where intermolecular interactions between unlike molecules lead to deviations from ideal behavior

9.3 Activity and activity coefficients

Activity and activity coefficients are key concepts in thermodynamics, helping us understand non-ideal behavior in mixtures. They quantify how components interact, affecting vapor pressure and equilibrium in solutions.

Standard states provide reference points for thermodynamic properties, while Raoult's and Henry's laws describe ideal solution behavior. Understanding these concepts is crucial for analyzing real-world mixtures and their deviations from ideality.

Activity and Standard States

Activity and Activity Coefficients

- Activity quantifies the effective concentration of a species in a mixture
- Accounts for non-ideal behavior and interactions between species
- Activity coefficient γ_i relates activity to mole fraction: $a_i = \gamma_i x_i$
- For ideal solutions, $\gamma_i = 1$ and activity equals mole fraction
- Activity coefficients depend on composition, temperature, and pressure

Standard States and Conventions

- Standard state is a reference condition for expressing thermodynamic properties
- For pure substances, standard state is the pure component at the system temperature and pressure
- For mixtures, standard state depends on the convention chosen
- Symmetrical convention defines standard state as the pure component at system temperature and pressure for all components
- Unsymmetrical convention defines standard state differently for solvent (pure liquid) and solutes (hypothetical ideal solution at unit molality)

Ideal Solution Laws

Raoult's Law for Ideal Solutions

- Raoult's law describes vapor-liquid equilibrium for ideal solutions
- Vapor pressure of each component is proportional to its mole fraction in the liquid phase: $p_i = x_i p_i^*$
- p_i^* is the vapor pressure of pure component i at the system temperature
- Applies to components that are liquid at the system temperature (typically the solvent)
- Examples: Benzene-toluene, ethanol-water (at low concentrations)

Henry's Law for Dilute Solutions

- Henry's law describes vapor-liquid equilibrium for dilute solutions
- Partial pressure of a solute is proportional to its mole fraction in the liquid phase: $p_i = H_i x_i$
- H_i is the Henry's law constant, which depends on temperature and solute-solvent pair
- Applies to components that are gases at the system temperature (typically solutes)
- Examples: Oxygen in water, carbon dioxide in beverages

Non-Ideal Solutions

Excess Gibbs Energy and Non-Ideality

- Non-ideal solutions deviate from ideal solution laws due to interactions between species
- Excess Gibbs energy G^E quantifies the deviation from ideal behavior: $G^E = G - G^{id}$
- G is the actual Gibbs energy of the mixture, and G^{id} is the Gibbs energy for an ideal mixture
- Activity coefficients relate excess Gibbs energy to composition: $\ln \gamma_i = \left(\frac{\partial(G^E/RT)}{\partial x_i} \right)_{T, P, x_j}$
- Positive G^E indicates positive deviations from ideality (repulsive interactions), while negative G^E indicates negative deviations (attractive interactions)

Examples of Non-Ideal Solutions

- Ethanol-water exhibits positive deviations from ideality at high concentrations due to hydrogen bonding
- Chloroform-acetone shows negative deviations from ideality due to strong intermolecular attractions
- Azeotropes are non-ideal mixtures with a composition where the vapor and liquid phases have the same composition at equilibrium
- Examples of azeotropes: Ethanol-water (95.6% ethanol), nitric acid-water (68% nitric acid)
- Non-ideal behavior is important in separation processes, as it affects vapor-liquid equilibrium and can limit separation efficiency

9.4 Excess properties and their relationships

Excess properties are crucial for understanding non-ideal mixtures in thermodynamics. They measure how real mixtures deviate from ideal behavior, helping us grasp the complex interactions between components. These properties are key to modeling and predicting the behavior of real-world fluid systems.

The Gibbs-Duhem equation and empirical models like Margules equations are essential tools for working with excess properties. They allow us to relate different excess properties and predict mixture behavior, bridging the gap between ideal theory and real-world applications in chemical engineering and related fields.

Excess Properties and Definitions

Understanding Excess Properties

- Excess properties quantify the deviation of a mixture's properties from ideal behavior
- Calculated as the difference between the actual property value and the value for an ideal solution
- Provide insights into the non-ideality of mixtures and the interactions between components
- Excess properties are denoted by the superscript "E" (e.g., G^E , H^E , S^E , V^E)
- Excess properties are extensive, meaning they depend on the amount of the mixture
- Excess properties are zero for ideal solutions and non-zero for non-ideal solutions

Key Excess Properties

- Excess Gibbs energy (G^E) represents the deviation of the Gibbs energy of mixing from ideal behavior
- Quantifies the non-ideality of a mixture in terms of the system's free energy
- Plays a central role in the thermodynamic description of non-ideal mixtures
- Excess enthalpy (H^E) represents the deviation of the enthalpy of mixing from ideal behavior
- Reflects the heat effects associated with the mixing process beyond ideal mixing
- Can be positive (endothermic mixing) or negative (exothermic mixing)
- Excess entropy (S^E) represents the deviation of the entropy of mixing from ideal behavior
- Quantifies the additional entropy changes due to non-ideal mixing

- Often negative due to increased order or reduced randomness in non-ideal mixtures
- Excess volume (V^E) represents the deviation of the volume of mixing from ideal behavior
- Indicates the volume changes that occur upon mixing beyond ideal mixing
- Can be positive (volume expansion) or negative (volume contraction)

Thermodynamic Relationships

Gibbs-Duhem Equation

- The Gibbs-Duhem equation is a fundamental thermodynamic relationship that connects the intensive properties of a mixture
- For a binary mixture at constant temperature and pressure, the Gibbs-Duhem equation is:
- $x_1 d\ln \gamma_1 + x_2 d\ln \gamma_2 = 0$
- x_1 and x_2 are the mole fractions of components 1 and 2
- γ_1 and γ_2 are the activity coefficients of components 1 and 2
- The Gibbs-Duhem equation imposes a constraint on the activity coefficients in a mixture
- If the activity coefficient of one component is known, the other can be determined using this equation
- The Gibbs-Duhem equation is useful in developing thermodynamic models and consistency tests for experimental data
- The equation can be extended to multicomponent systems and other types of intensive properties (e.g., partial molar volumes, partial molar enthalpies)

Empirical Models for Excess Gibbs Energy

Two-Suffix Margules Equations

- The Margules equations are empirical models used to represent the excess Gibbs energy of binary mixtures
- The two-suffix Margules equation is:
- $\frac{G^E}{RT} = x_1 x_2 (A_{12} + 2(A_{21} - A_{12})x_1)$
- A_{12} and A_{21} are adjustable parameters specific to the binary mixture
- The two-suffix Margules equation is symmetric, meaning it treats both components equally
- The equation can capture simple non-ideal behavior and is suitable for mixtures with moderate deviations from ideality

Three-Suffix Margules Equation

- The three-suffix Margules equation is an extension of the two-suffix equation, incorporating an additional adjustable parameter
- $\frac{G^E}{RT} = x_1 x_2 (A_{12} + 2(A_{21} - A_{12})x_1 + 3(A_{12} - 2A_{21} + A_{22})x_1^2)$
- A_{12} , A_{21} , and A_{22} are adjustable parameters specific to the binary mixture

- The three-suffix Margules equation can capture more complex non-ideal behavior compared to the two-suffix equation
- The equation is asymmetric, allowing for different contributions from each component to the excess Gibbs energy

Other Empirical Models

- Van Laar equation: An empirical model for the excess Gibbs energy based on the concept of regular solutions

$$\frac{G^E}{RT} = \frac{A_{12}X_1}{1 + \frac{A_{12}X_1}{A_{21}X_2}} + \frac{A_{21}X_2}{1 + \frac{A_{21}X_2}{A_{12}X_1}}$$

- A_{12} and A_{21} are adjustable parameters specific to the binary mixture
- Wilson equation: An empirical model that accounts for local composition effects and differences in molecular size and interaction energies
- $\frac{G^E}{RT} = -x_1 \ln(x_1 + \Lambda_{12}x_2) - x_2 \ln(x_2 + \Lambda_{21}x_1)$
- Λ_{12} and Λ_{21} are adjustable parameters related to the interaction energies and molar volumes of the components
- NRTL (Non-Random Two-Liquid) equation: An empirical model that considers the non-randomness of molecular interactions in the liquid phase

$$\frac{G^E}{RT} = x_1x_2\left(\frac{\tau_{21}G_{21}}{x_1 + x_2G_{21}} + \frac{\tau_{12}G_{12}}{x_2 + x_1G_{12}}\right)$$

- τ_{12} , τ_{21} , G_{12} , and G_{21} are adjustable parameters related to the interaction energies and the non-randomness factor
- UNIQUAC (Universal Quasi-Chemical) model: An empirical model that accounts for the combinatorial entropy and the energetic interactions between molecules
- Consists of a combinatorial term and a residual term
- Requires pure component parameters (volume and surface area parameters) and binary interaction parameters
- Suitable for a wide range of mixtures, including those with polar and associating components

Unit 10 – Vapor–Liquid Equilibrium

10.1 Raoult's law and Henry's law

Raoult's law and Henry's law are key concepts in vapor-liquid equilibrium. They help us understand how different components in a mixture behave under various conditions. These laws are crucial for predicting the behavior of ideal and dilute solutions.

These laws have practical applications in many fields. From distillation processes in chemical engineering to understanding gas solubility in environmental science, they provide a foundation for analyzing and designing systems involving liquid-vapor interactions.

Raoult's Law and Ideal Solutions

Raoult's Law and Vapor Pressure

- Raoult's law states the partial vapor pressure of each component in an ideal mixture is equal to the vapor pressure of the pure component multiplied by its mole fraction in the mixture
- Partial pressure refers to the pressure that each individual component of a mixture would exert if it occupied the same volume alone at the same temperature
- Vapor pressure is the pressure exerted by a vapor in thermodynamic equilibrium with its condensed phases (solid or liquid) at a given temperature in a closed system
- Raoult's law applies to ideal solutions where the interactions between molecules of different components are similar to those between molecules of the same component
- Mathematically, Raoult's law can be expressed as $p_i = x_i p_i^*$, where p_i is the partial vapor pressure of component i , x_i is the mole fraction of component i in the liquid mixture, and p_i^* is the vapor pressure of pure component i

Ideal Solutions and Mole Fractions

- An ideal solution is a solution in which the enthalpy of mixing is zero and the activity coefficients are equal to one
- In an ideal solution, the interactions between molecules of different components are the same as those between molecules of the same component
- The mole fraction is the ratio of moles of one component to the total moles of all components in a mixture
- For a binary mixture, the mole fractions of components 1 and 2 are given by $x_1 = \frac{n_1}{n_1 + n_2}$ and $x_2 = \frac{n_2}{n_1 + n_2}$, where n_1 and n_2 are the number of moles of components 1 and 2, respectively
- The sum of mole fractions for all components in a mixture always equals one ($x_1 + x_2 = 1$ for a binary mixture)

Henry's Law and Dilute Solutions

Henry's Law and Solubility

- Henry's law states that at a constant temperature, the amount of a given gas dissolved in a liquid is directly proportional to the partial pressure of that gas in equilibrium with that liquid
- Mathematically, Henry's law is expressed as $P = k_H C$, where P is the partial pressure of the gas above the solution, C is the concentration of the gas in the solution, and k_H is Henry's law constant, which depends on the solute, solvent, and temperature
- Henry's law is most accurate for dilute solutions, where the dissolved gas is at a low concentration and behaves ideally
- The solubility of a gas in a liquid increases with increasing pressure and decreases with increasing temperature (for gases that do not react chemically with the solvent)
- Examples of gases that follow Henry's law include oxygen, nitrogen, and carbon dioxide dissolved in water at low concentrations

Solutes, Solvents, and Dilute Solutions

- A solute is the substance that is dissolved in a solution, typically present in a smaller amount than the solvent
- A solvent is the substance in which the solute is dissolved, typically present in a larger amount than the solute
- In a dilute solution, the solute is present at a low concentration relative to the solvent
- Dilute solutions exhibit properties that are close to those of the pure solvent, as the solute molecules are far apart and interact mainly with the solvent molecules
- Examples of dilute solutions include a small amount of sugar dissolved in water or a low concentration of salt in water

10.2 VLE calculations for ideal and non-ideal mixtures

Vapor-liquid equilibrium (VLE) calculations are crucial for understanding how mixtures behave. They help us predict when liquids will boil or vapors will condense, which is super important in chemical engineering and industry.

We'll look at ideal and non-ideal mixtures, and how they differ. We'll also check out VLE diagrams and activity coefficient models. These tools help us figure out what's happening in complex mixtures, like in distillation columns or chemical reactors.

Ideal and Non-ideal Mixtures

Characteristics and Behavior of Mixtures

- Ideal mixture exhibits no enthalpy change upon mixing and follows Raoult's law
- Non-ideal mixture deviates from Raoult's law due to molecular interactions between different species
- Activity coefficient (γ_i) quantifies the deviation from ideal behavior for each component in a mixture

- For an ideal mixture, $\gamma_i = 1$
- In a non-ideal mixture, $\gamma_i \neq 1$ and varies with composition and temperature
- Fugacity ($\hat{f}_i$) represents the effective partial pressure of a component in a mixture
- For an ideal mixture, fugacity equals the partial pressure ($\hat{f}_i = y_i P$)
- In a non-ideal mixture, fugacity is related to the activity coefficient and vapor pressure ($\hat{f}_i = \gamma_i x_i P_i^{sat}$)

Thermodynamic Relationships in Mixtures

- Gibbs-Duhem equation relates changes in chemical potential, temperature, and pressure for a mixture at equilibrium
- For a binary mixture: $x_1 d\ln(\gamma_1) + x_2 d\ln(\gamma_2) = 0$
- Constrains the behavior of activity coefficients in a mixture
- Allows the calculation of one activity coefficient if the other is known

VLE Diagrams

Types of VLE Diagrams

- Vapor-liquid equilibrium (VLE) diagrams represent the composition of coexisting vapor and liquid phases at equilibrium
- T-x-y diagram displays the relationship between temperature and composition at a fixed pressure
- x represents the liquid phase mole fraction
- y represents the vapor phase mole fraction
- Bubble point curve connects the liquid compositions in equilibrium with their corresponding vapor compositions
- Dew point curve connects the vapor compositions in equilibrium with their corresponding liquid compositions
- P-x-y diagram shows the relationship between pressure and composition at a fixed temperature
- Similar to the T-x-y diagram, with pressure on the vertical axis instead of temperature

Key Points on VLE Diagrams

- Bubble point represents the temperature (or pressure) at which the first vapor bubble forms upon heating a liquid mixture
- Determined by the intersection of a vertical line (fixed x) with the bubble point curve
- Dew point represents the temperature (or pressure) at which the first liquid droplet forms upon cooling a vapor mixture
- Determined by the intersection of a vertical line (fixed y) with the dew point curve
- VLE diagrams are essential for designing separation processes (distillation) and understanding the behavior of mixtures

Activity Coefficient Models

Overview of Activity Coefficient Models

- Activity coefficient models estimate the non-ideal behavior of mixtures based on molecular interactions and composition
- Wilson equation is a semi-empirical model that accounts for local composition effects
- Assumes that the local composition around a molecule differs from the overall mixture composition
- Requires binary interaction parameters, which are often temperature-dependent
- NRTL (Non-Random Two-Liquid) model is an extension of the Wilson equation that includes a non-randomness parameter
- Accounts for the non-random distribution of molecules in a mixture
- Requires binary interaction parameters and a non-randomness factor (typically set to 0.3 or 0.4)

UNIQUAC Model

- UNIQUAC (UNiversal QUAsiChemical) model is a more complex activity coefficient model that considers both combinatorial and residual contributions
- Combinatorial term accounts for the size and shape differences between molecules
- Residual term accounts for the energetic interactions between molecules
- UNIQUAC model requires pure component parameters (volume and surface area) and binary interaction parameters
- Widely used in the chemical industry for modeling non-ideal mixtures, particularly those containing polar or associating compounds (alcohols, acids)

10.3 Flash calculations and distillation principles

Flash calculations and distillation principles are key concepts in vapor-liquid equilibrium. They help us understand how to separate liquid mixtures into vapor and liquid phases, which is crucial for many industrial processes.

These techniques rely on equilibrium ratios and relative volatility to determine how easily components can be separated. By applying these principles, we can design effective distillation columns and optimize separation processes in chemical engineering.

Flash Calculations

Flash Distillation Process

- Flash distillation separates a liquid mixture into vapor and liquid phases by reducing pressure or increasing temperature
- Occurs in a flash drum, a vessel designed to facilitate the rapid vaporization of a portion of the liquid feed
- Feed composition determines the initial mixture of components entering the flash drum

- Vapor fraction represents the proportion of the feed that vaporizes during the flash process
- Liquid fraction represents the proportion of the feed that remains in the liquid phase after flashing

Equilibrium and Rachford-Rice Equation

- Equilibrium ratio (K-value) measures the tendency of a component to partition between the vapor and liquid phases at equilibrium
- K-values depend on temperature, pressure, and the nature of the components in the mixture
- Rachford-Rice equation is used to calculate the vapor and liquid fractions in a flash calculation
- Relates the feed composition, K-values, and vapor fraction
- Solved iteratively to determine the vapor fraction that satisfies the material balance
- Example: In a flash calculation for a binary mixture of ethane and propane, the Rachford-Rice equation is used to determine the vapor and liquid fractions at a given temperature and pressure

Distillation Principles

Relative Volatility and Separation

- Relative volatility measures the ease of separating two components in a mixture by distillation
- Defined as the ratio of the K-values of the more volatile component to the less volatile component
- Higher relative volatility indicates a more accessible separation (e.g., ethane and hexane)
- Lower relative volatility indicates a more challenging separation (e.g., benzene and toluene)
- Distillation columns are used to separate mixtures based on differences in volatility
- Consist of a vertical tower with multiple stages or trays
- Liquid flows down the column while vapor flows up, allowing for mass transfer between phases

Theoretical Stages and Column Design

- Theoretical stages represent the equilibrium contacts between vapor and liquid phases in a distillation column
- Each stage assumes perfect mixing and equilibrium between the vapor and liquid leaving the stage
- Actual distillation columns require more stages than theoretical due to non-ideal mixing and mass transfer limitations
- Number of theoretical stages required for a given separation depends on the relative volatility and desired product purities
- More stages are needed for lower relative volatility or higher purity requirements
- Example: In the design of a distillation column for separating ethanol and water, the number of theoretical stages is determined based on the desired ethanol purity in the distillate and the relative volatility of ethanol to water at the operating conditions

10.4 Azeotropes and their significance

Azeotropes are mixtures of liquids that boil at a constant temperature and composition, behaving like pure components during distillation. They're crucial in vapor-liquid equilibrium because they can't be separated by simple distillation, posing challenges in industrial processes.

Understanding azeotropes is key to designing effective separation techniques. This section covers types of azeotropes, their properties, and separation methods like azeotropic distillation, extractive distillation, and pressure-swing distillation, which are essential for overcoming azeotropic limitations in industry.

Types of Azeotropes

Definition and Characteristics of Azeotropes

- Azeotrope
- Mixture of two or more liquids that boils at a constant temperature and composition
- Vapor and liquid compositions are the same at the azeotropic point
- Behaves like a pure component during boiling and condensation
- Cannot be separated by simple distillation (ethanol-water azeotrope)

Classification Based on Boiling Point Deviation

- Positive azeotrope
- Exhibits a maximum boiling point compared to the pure components
- Boiling point is higher than that of either pure component at the same pressure
- Vapor pressure of the mixture is lower than expected from Raoult's law (ethanol-water, nitric acid-water)
- Negative azeotrope
- Exhibits a minimum boiling point compared to the pure components
- Boiling point is lower than that of either pure component at the same pressure
- Vapor pressure of the mixture is higher than expected from Raoult's law (acetone-chloroform, methanol-benzene)

Classification Based on Phase Behavior

- Homogeneous azeotrope
- Azeotropic mixture forms a single liquid phase
- Components are miscible in all proportions (ethanol-water, acetone-methanol)
- Heterogeneous azeotrope
- Azeotropic mixture forms two or more liquid phases
- Components have limited miscibility (water-toluene, water-butyl acetate)
- Decantation can be used to separate the phases after condensation

Azeotropic Properties

Composition and Boiling Point

- Azeotropic composition
- Specific mole fractions or mass fractions of components at which the azeotrope occurs
- Depends on the system pressure and temperature
- Can be determined experimentally or predicted using vapor-liquid equilibrium models (NRTL, UNIQUAC)
- Azeotropic composition shifts with changes in pressure (ethanol-water: 95.6% ethanol at 1 atm)

Vapor-Liquid Equilibrium Behavior

- Azeotropic systems exhibit non-ideal vapor-liquid equilibrium behavior
- Deviations from Raoult's law due to intermolecular interactions between components
- Activity coefficients are used to account for non-ideality in thermodynamic models
- Azeotropic point represents a singular point in the vapor-liquid equilibrium diagram
- Vapor and liquid compositions are equal at the azeotropic point
- Tie lines converge at the azeotropic point in xy and Txy diagrams

Azeotropic Separation Techniques

Azeotropic Distillation

- Azeotropic distillation
- Separation technique that uses an entrainer to alter the relative volatility of components
- Entrainers form a new azeotrope with one or more components, facilitating separation
- Distillate or bottoms product contains the desired component (ethanol dehydration using benzene)
- Entrainers selection is crucial for effective azeotropic distillation
- Should form a heterogeneous azeotrope with one of the components
- Entrainers should be easily separable from the desired product
- Commonly used entrainers include benzene, cyclohexane, and pentane

Extractive Distillation

- Extractive distillation
- Separation technique that uses a high-boiling solvent to alter the relative volatility of components
- Solvent interacts differently with the components, enhancing their separation
- Solvent is introduced at a higher stage in the distillation column (ethanol dehydration using ethylene glycol)

- Solvent selection criteria for extractive distillation
- High boiling point to facilitate recovery and recycling
- Selective interaction with one of the components
- Low volatility to minimize solvent loss in the distillate
- Examples of solvents: ethylene glycol, glycerol, and ionic liquids

Pressure-Swing Distillation

- Pressure-swing distillation
- Separation technique that exploits the pressure dependence of azeotropic composition
- Two distillation columns operating at different pressures are used
- Azeotropic composition shifts, allowing for separation of components (acetone-methanol separation)
- Advantages of pressure-swing distillation
- Avoids the use of additional components (entrainers or solvents)
- Reduced energy consumption compared to other azeotropic separation techniques
- Suitable for heat-sensitive components due to lower operating temperatures

Unit 11 – Solution Thermodynamics

11.1 Partial molar properties

Partial molar properties are key to understanding how components behave in mixtures. They show how adding a bit of one substance changes the overall properties of the whole mix. This helps predict how mixtures will act under different conditions.

These properties, like partial molar volume and Gibbs free energy, are crucial for calculating changes in mixtures. They're especially useful when dealing with real-world solutions, where components interact in complex ways. Understanding these concepts is vital for solving practical problems in thermodynamics.

Partial Molar Quantities

Definition and Significance

- Partial molar quantities represent the contribution of each component to the total thermodynamic property of a mixture
- Useful for understanding the behavior and properties of individual components in a mixture
- Allow for the calculation of changes in thermodynamic properties when the composition of a mixture is altered

Types of Partial Molar Quantities

- Partial molar volume
 - Represents the change in volume of a mixture when one mole of a component is added at constant temperature, pressure, and composition
 - Calculated using the equation $\bar{V}_i = \left(\frac{\partial V}{\partial n_i}\right)_{T, P, n_j}$
- Partial molar Gibbs free energy
 - Represents the change in Gibbs free energy of a mixture when one mole of a component is added at constant temperature, pressure, and composition
 - Equivalent to the chemical potential of the component in the mixture
 - Calculated using the equation $\bar{G}_i = \left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_j}$
- Partial molar enthalpy
 - Represents the change in enthalpy of a mixture when one mole of a component is added at constant temperature, pressure, and composition
 - Calculated using the equation $\bar{H}_i = \left(\frac{\partial H}{\partial n_i}\right)_{T, P, n_j}$

Chemical Potential

- Chemical potential is the partial molar Gibbs free energy of a component in a mixture
- Represents the change in Gibbs free energy when one mole of a component is added to a mixture at constant temperature, pressure, and composition

- Determines the direction of chemical reactions and phase transitions in a mixture
- Equals the molar Gibbs free energy for pure substances

Thermodynamic Relationships

Gibbs-Duhem Equation

- Relates changes in chemical potentials of components in a mixture to changes in temperature and pressure
- Constrains the values of partial molar quantities in a mixture
- Expressed as

$$\sum_{i=1}^n x_i d\mu_i = -SdT + VdP$$

, where x_i is the mole fraction, μ_i is the chemical potential, S is the entropy, T is the temperature, V is the volume, and P is the pressure

Relationship between Chemical Potential and Partial Molar Gibbs Free Energy

- Chemical potential and partial molar Gibbs free energy are equivalent for a component in a mixture
- $\mu_i = \bar{G}_i = \left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_j}$
- Allows for the calculation of chemical potentials from Gibbs free energy data and vice versa

Applications of Thermodynamic Relationships

- Predicting the behavior of mixtures under different conditions (temperature, pressure, composition)
- Calculating changes in thermodynamic properties during mixing or separation processes
- Determining the equilibrium composition of a mixture based on chemical potentials

Composition Variables

Molality

- Molality (m) is the number of moles of solute per kilogram of solvent
- Expressed as $m = \frac{n_{\text{solute}}}{m_{\text{solvent}}}$, where n_{solute} is the number of moles of solute and m_{solvent} is the mass of solvent in kilograms
- Molality is independent of temperature and pressure, making it a useful composition variable for thermodynamic calculations

Mole Fraction

- Mole fraction (x) is the ratio of the number of moles of a component to the total number of moles in a mixture
- Expressed as

$$x_i = \frac{n_i}{\sum_{i=1}^n n_i}$$

, where n_i is the number of moles of component i and

$$\sum_{i=1}^n n_i$$

is the total number of moles in the mixture

- Mole fractions are dimensionless and sum to unity for all components in a mixture

Relationship between Composition Variables and Chemical Potential

- Chemical potential of a component in a mixture depends on its composition
- For ideal solutions, the chemical potential is related to the mole fraction by $\mu_i = \mu_i^0 + RT \ln x_i$, where μ_i^0 is the standard chemical potential, R is the gas constant, and T is the temperature
- Composition variables allow for the calculation of chemical potentials and the prediction of mixture behavior based on composition changes

11.2 Ideal and non-ideal solutions

Solutions can be ideal or non-ideal, affecting their behavior. Ideal solutions follow Raoult's and Henry's laws, assuming no interactions between components. Non-ideal solutions deviate from these laws due to molecular interactions, requiring activity coefficients and excess properties to describe their behavior.

Models like regular solutions, Van Laar, and Margules equations help predict non-ideal solution behavior. These models use parameters to account for deviations from ideality, allowing for more accurate predictions of thermodynamic properties in real-world applications.

Ideal Solutions

Raoult's Law

- Describes the vapor pressure of an ideal solution
- States that the partial vapor pressure of each component in an ideal solution is equal to the vapor pressure of the pure component multiplied by its mole fraction in the solution
- Mathematically expressed as $p_i = x_i p_i^*$, where p_i is the partial vapor pressure of component i , x_i is the mole fraction of component i , and p_i^* is the vapor pressure of pure component i
- Assumes no intermolecular interactions between different components in the solution
- Applicable to solutions where the components have similar molecular sizes and intermolecular forces (ethanol and water)

Henry's Law

- Describes the solubility of a gas in a liquid at a given temperature
- States that the amount of dissolved gas is directly proportional to the partial pressure of the gas above the liquid
- Mathematically expressed as $C = kP$, where C is the concentration of the dissolved gas, P is the partial pressure of the gas, and k is Henry's law constant, which depends on the solute, solvent, and

temperature

- Assumes that the gas molecules do not interact with each other in the solution
- Applicable to dilute solutions where the solute is a gas and the solvent is a liquid (carbon dioxide in water)

Non-Ideal Solutions

Activity Coefficient

- A factor that accounts for the deviation of a solution from ideal behavior
- Defined as the ratio of the actual fugacity (or activity) of a component to its ideal fugacity (or activity)
- Mathematically expressed as $\gamma_i = \frac{f_i}{x_i f_i^*}$, where γ_i is the activity coefficient of component i , f_i is the fugacity of component i in the solution, x_i is the mole fraction of component i , and f_i^* is the fugacity of pure component i
- A value of 1 indicates ideal behavior, while values greater than 1 indicate positive deviations and values less than 1 indicate negative deviations from ideality
- Depends on the composition of the solution and the intermolecular interactions between components (ethanol and water at high concentrations)

Excess Properties

- Thermodynamic properties that describe the deviation of a solution from ideal behavior
- Defined as the difference between the actual value of a property and the value it would have in an ideal solution
- Examples include excess Gibbs free energy (G^E), excess enthalpy (H^E), and excess entropy (S^E)
- Mathematically expressed as $M^E = M - M^{id}$, where M^E is the excess property, M is the actual value of the property, and M^{id} is the value of the property in an ideal solution
- Provide insights into the nature and strength of intermolecular interactions in the solution (mixing of ethanol and water results in a negative excess enthalpy)

Deviation from Ideality

- Occurs when the properties of a solution deviate from those predicted by ideal solution laws (Raoult's law and Henry's law)
- Can be caused by differences in molecular size, shape, or intermolecular forces between components
- Positive deviations occur when the intermolecular attractions between unlike molecules are weaker than those between like molecules, leading to higher vapor pressures and lower boiling points than predicted (acetone and chloroform)
- Negative deviations occur when the intermolecular attractions between unlike molecules are stronger than those between like molecules, leading to lower vapor pressures and higher boiling points than predicted (chloroform and ethanol)
- The extent of deviation depends on the nature and concentration of the components in the solution

Models for Non-Ideal Solutions

Regular Solutions

- A model that accounts for the non-ideality of solutions caused by differences in intermolecular forces between components
- Assumes that the excess entropy of mixing is zero ($S^E = 0$) and that the excess enthalpy of mixing is proportional to the product of the mole fractions of the components
- Mathematically expressed as $G^E = x_1x_2\Lambda$, where G^E is the excess Gibbs free energy, x_1 and x_2 are the mole fractions of components 1 and 2, and Λ is a parameter that depends on the intermolecular interactions between the components
- Provides a simple way to estimate the activity coefficients and vapor-liquid equilibrium of non-ideal solutions (hexane and benzene)
- Limited to solutions where the components have similar molecular sizes and shapes

Van Laar Equation

- An empirical model that describes the excess Gibbs free energy of non-ideal solutions
- Assumes that the excess Gibbs free energy is a function of the mole fractions and two adjustable parameters, A and B
- Mathematically expressed as $\frac{G^E}{RT} = \frac{Ax_1x_2}{x_1 + Bx_2} + \frac{Bx_1x_2}{Bx_1 + x_2}$, where G^E is the excess Gibbs free energy, R is the gas constant, T is the temperature, x_1 and x_2 are the mole fractions of components 1 and 2, and A and B are adjustable parameters that depend on the components and temperature
- Provides a better fit to experimental data than the regular solution model for solutions with moderate deviations from ideality (ethanol and water)
- Requires the determination of the adjustable parameters from experimental data

Margules Equation

- An empirical model that describes the excess Gibbs free energy of non-ideal solutions
- Assumes that the excess Gibbs free energy is a polynomial function of the mole fractions and adjustable parameters
- The two-suffix Margules equation is mathematically expressed as $\frac{G^E}{RT} = x_1x_2(A_{12} + B_{12}(x_1 - x_2))$, where G^E is the excess Gibbs free energy, R is the gas constant, T is the temperature, x_1 and x_2 are the mole fractions of components 1 and 2, and A_{12} and B_{12} are adjustable parameters that depend on the components and temperature
- The three-suffix Margules equation includes an additional term with a third adjustable parameter to better describe solutions with large deviations from ideality (acetone and chloroform)
- Provides a flexible and accurate way to model the thermodynamic properties of non-ideal solutions
- Requires the determination of the adjustable parameters from experimental data

11.3 Mixing processes and heat effects

Mixing processes in thermodynamics involve combining substances and analyzing the resulting energy changes. These processes can be endothermic or exothermic, affecting the system's temperature and overall energy state.

Understanding mixing processes is crucial for grasping solution thermodynamics. By examining enthalpy, entropy, and Gibbs free energy of mixing, we can predict the spontaneity and heat effects of various mixing scenarios in real-world applications.

Thermodynamic Properties of Mixing

Enthalpy and Entropy of Mixing

- Enthalpy of mixing (ΔH_{mix}) represents the change in enthalpy when two or more substances are mixed together at constant temperature and pressure
- Can be positive (endothermic) or negative (exothermic) depending on the interactions between the components
- For ideal solutions, $\Delta H_{mix} = 0$ because there are no interactions between the components
- Entropy of mixing (ΔS_{mix}) quantifies the increase in disorder or randomness when substances are mixed together
- Always positive for mixing processes because mixing increases the randomness of the system
- For ideal solutions, $\Delta S_{mix} = -R \sum x_i \ln x_i$, where R is the gas constant and x_i is the mole fraction of component i

Gibbs Free Energy and Excess Enthalpy

- Gibbs free energy of mixing (ΔG_{mix}) determines the spontaneity of the mixing process at constant temperature and pressure
- Calculated using the equation $\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$
- Mixing is spontaneous when $\Delta G_{mix} < 0$, non-spontaneous when $\Delta G_{mix} > 0$, and at equilibrium when $\Delta G_{mix} = 0$
- Excess enthalpy (H^E) is the difference between the actual enthalpy of mixing and the enthalpy of mixing for an ideal solution
- Accounts for the non-ideal interactions between the components in a real solution
- Positive H^E indicates stronger interactions between like molecules (endothermic), while negative H^E indicates stronger interactions between unlike molecules (exothermic)
- For ideal solutions, $H^E = 0$ because there are no non-ideal interactions

Heat Effects in Mixing Processes

Heat of Solution

- Heat of solution (ΔH_{sol}) is the enthalpy change associated with dissolving a solute in a solvent to form a solution

- Can be positive (endothermic) or negative (exothermic) depending on the interactions between the solute and solvent
- Endothermic heat of solution (positive ΔH_{sol}) occurs when the energy required to break solute-solute and solvent-solvent interactions is greater than the energy released from forming solute-solvent interactions (e.g., dissolving ammonium nitrate in water)
- Exothermic heat of solution (negative ΔH_{sol}) occurs when the energy released from forming solute-solvent interactions is greater than the energy required to break solute-solute and solvent-solvent interactions (e.g., dissolving sodium hydroxide in water)

Endothermic and Exothermic Mixing

- Endothermic mixing processes absorb heat from the surroundings, resulting in a decrease in temperature
- Occurs when the interactions between the components being mixed are weaker than the interactions within the pure components
- Examples include mixing ethanol and water, where the temperature of the mixture decreases due to the breaking of hydrogen bonds in the pure components
- Exothermic mixing processes release heat to the surroundings, resulting in an increase in temperature
- Occurs when the interactions between the components being mixed are stronger than the interactions within the pure components
- Examples include mixing sulfuric acid and water, where the temperature of the mixture increases due to the formation of strong interactions between the acid and water molecules

11.4 Liquid-liquid and solid-liquid equilibria

Liquid-liquid and solid-liquid equilibria are crucial concepts in solution thermodynamics. They help us understand how different substances mix and separate, which is key for many industrial processes and everyday phenomena.

These equilibria involve phase diagrams, miscibility gaps, and critical solution temperatures. We'll explore how to determine compositions using the lever rule and tie lines, and dive into solubility curves and colligative properties.

Phase Equilibria Fundamentals

Phase Diagrams and Miscibility Gaps

- Phase diagrams graphically represent the equilibrium states of a system as a function of temperature, pressure, and composition
- Provide information about the phases present at different conditions (solid, liquid, gas)
- Help predict the behavior of mixtures and the conditions at which phase transitions occur
- Miscibility gaps represent regions on a phase diagram where two liquid phases coexist in equilibrium
- Occur when the components of a mixture have limited solubility in each other
- The mixture separates into two distinct liquid layers with different compositions (oil and water)

Critical Solution Temperature and Eutectic Points

- Critical solution temperature (CST) is the temperature above or below which a mixture becomes completely miscible
- Upper critical solution temperature (UCST): the mixture is miscible above this temperature and separates into two phases below it (nitrobenzene and hexane)
- Lower critical solution temperature (LCST): the mixture is miscible below this temperature and separates into two phases above it (triethylamine and water)
- Eutectic points represent the lowest temperature and composition at which a mixture of solid phases can coexist in equilibrium with a liquid phase
- At the eutectic point, the solid phases melt simultaneously, forming a liquid with the eutectic composition
- Eutectic mixtures have a lower melting point than the individual components (lead-tin solder)

Composition Determination

Lever Rule and Tie Lines

- The lever rule is used to determine the relative amounts of phases present in a two-phase region of a phase diagram
- The ratio of the distances from a point in the two-phase region to the phase boundaries is inversely proportional to the ratio of the amounts of each phase present
- Allows for the calculation of the mass fractions or mole fractions of each phase at equilibrium
- Tie lines connect the compositions of coexisting phases in a two-phase region
- Represent the equilibrium compositions of the phases at a given temperature and pressure
- The endpoints of a tie line lie on the phase boundaries and indicate the compositions of the individual phases (liquid and vapor in a vapor-liquid equilibrium)

Solubility Curves

- Solubility curves represent the maximum amount of a solute that can dissolve in a solvent at a given temperature
- Show the temperature dependence of solubility for a particular solute-solvent system
- The area below the solubility curve represents the conditions under which the solution is unsaturated, while the area above the curve represents supersaturation (sugar in water)
- The shape of the solubility curve depends on the nature of the solute and solvent interactions
- Some solutes exhibit increasing solubility with temperature (most salts in water), while others show decreasing solubility (calcium hydroxide in water)
- Solubility curves help determine the conditions required for crystallization or precipitation of a solute from a solution

Colligative Properties

Freezing Point Depression and Boiling Point Elevation

- Colligative properties are properties of solutions that depend on the concentration of the solute particles, but not on their identity
- Include freezing point depression, boiling point elevation, vapor pressure lowering, and osmotic pressure
- These properties arise from the change in the chemical potential of the solvent due to the presence of the solute
- Freezing point depression is the lowering of the freezing point of a solvent when a non-volatile solute is added
- The magnitude of the depression is proportional to the molal concentration of the solute (salt in water)
- Freezing point depression is used in applications such as antifreeze in automotive cooling systems and the production of ice cream
- Boiling point elevation is the increase in the boiling point of a solvent when a non-volatile solute is added
- The magnitude of the elevation is proportional to the molal concentration of the solute (ethylene glycol in water)
- Boiling point elevation is used in applications such as the production of concentrated solutions and the purification of solvents through distillation

Unit 12 – Chemical Reaction Equilibria

12.1 Thermodynamics of chemical reactions

Chemical reactions are the heart of many processes in nature and industry. Understanding their thermodynamics helps us predict if they'll happen on their own or need a push. We'll look at key concepts like Gibbs free energy, enthalpy, and entropy.

We'll also explore how reactions progress, from start to finish. This includes energy profiles, reaction coordinates, and what happens when reactions reach equilibrium. These ideas are crucial for grasping chemical reaction equilibria.

Thermodynamic Quantities

Gibbs Free Energy and Spontaneity

- Gibbs free energy (G) measures the maximum reversible work that can be performed by a system at constant temperature and pressure
- Changes in Gibbs free energy (ΔG) determine the spontaneity of a process
- If $\Delta G < 0$, the process is spontaneous and will occur naturally
- If $\Delta G > 0$, the process is non-spontaneous and requires an input of energy to proceed
- If $\Delta G = 0$, the system is at equilibrium, and no net change occurs
- Gibbs free energy is related to enthalpy (H) and entropy (S) by the equation: $G = H - TS$, where T is the absolute temperature

Enthalpy and Heat of Reaction

- Enthalpy (H) is a state function that represents the total heat content of a system
- Changes in enthalpy (ΔH) during a chemical reaction are known as the heat of reaction
- For an exothermic reaction, $\Delta H < 0$, indicating heat is released by the system to the surroundings
- For an endothermic reaction, $\Delta H > 0$, indicating heat is absorbed by the system from the surroundings
- The heat of reaction can be measured using calorimetry experiments (constant-pressure calorimetry)
- Hess's law states that the total enthalpy change for a reaction is independent of the pathway and depends only on the initial and final states

Entropy and Spontaneity

- Entropy (S) is a measure of the disorder or randomness of a system
- According to the second law of thermodynamics, the entropy of the universe always increases for a spontaneous process
- Changes in entropy (ΔS) contribute to the spontaneity of a process
- If $\Delta S > 0$, the process is spontaneous and will occur naturally

- If $\Delta S < 0$, the process is non-spontaneous and requires an input of energy to proceed
- Entropy increases with increasing temperature, volume, and the number of particles in a system (ideal gas equation)

Reaction Dynamics

Reaction Coordinate and Energy Profile

- A reaction coordinate is a geometric parameter that describes the progress of a chemical reaction from reactants to products
- An energy profile is a plot of the potential energy of the system as a function of the reaction coordinate
- The energy profile shows the activation energy barrier that must be overcome for the reaction to proceed
- The difference in potential energy between the reactants and products represents the heat of reaction (ΔH)
- Catalysts lower the activation energy barrier without being consumed in the reaction, increasing the reaction rate (enzymes in biological systems)

Spontaneity and Thermodynamic Equilibrium

- The spontaneity of a reaction is determined by the sign of ΔG , which depends on both ΔH and ΔS
- A reaction will proceed spontaneously in the direction that decreases Gibbs free energy until equilibrium is reached
- At thermodynamic equilibrium, $\Delta G = 0$, and the forward and reverse reaction rates are equal
- The equilibrium constant (K) is related to the standard Gibbs free energy change (ΔG°) by the equation: $\Delta G^\circ = -RT \ln K$, where R is the gas constant and T is the absolute temperature
- The equilibrium position can be shifted by changing the temperature, pressure, or concentrations of reactants or products (Le Chatelier's principle)

Reference States

Standard State and Standard Thermodynamic Quantities

- The standard state of a substance is defined as the pure substance at a pressure of 1 atm (or 1 bar) and a specified temperature (usually 25°C or 298 K)
- Standard thermodynamic quantities, such as standard enthalpy of formation (ΔH_f°), standard entropy (S°), and standard Gibbs free energy of formation (ΔG_f°), are defined for substances in their standard states
- These values are used to calculate the standard enthalpy change (ΔH°), standard entropy change (ΔS°), and standard Gibbs free energy change (ΔG°) for a reaction
- Standard thermodynamic quantities can be found in reference tables (thermodynamic tables) and are essential for predicting the spontaneity and equilibrium of chemical reactions under standard conditions
- The standard heat of formation (ΔH_f°) is the enthalpy change when one mole of a compound is formed from its constituent elements in their standard states (Hess's law)

12.2 Equilibrium constants and their temperature dependence

Chemical reactions reach a balance between reactants and products called equilibrium. Equilibrium constants measure this balance, showing how much product forms compared to reactants. The constant's value depends on temperature, which affects whether reactions favor products or reactants.

Understanding equilibrium constants helps predict how reactions behave under different conditions. Temperature changes can shift the balance, influencing product yields. This knowledge is key for optimizing chemical processes in industry and understanding natural chemical systems.

Equilibrium Constant and Law of Mass Action

Defining Equilibrium Constant

- Equilibrium constant (K) quantifies the relationship between reactants and products at equilibrium
- Determined by the ratio of product concentrations to reactant concentrations, each raised to their stoichiometric coefficients
- For a general reaction $aA + bB \rightleftharpoons cC + dD$, the equilibrium constant is expressed as: $K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$
- Square brackets denote molar concentrations (molarity) of the respective species at equilibrium
- Equilibrium constants are dimensionless quantities, as the units of concentration cancel out

Law of Mass Action

- The law of mass action states that at equilibrium, the ratio of the product of the concentrations of the products to the product of the concentrations of the reactants, each raised to a power equal to its stoichiometric coefficient, is a constant at a given temperature
- Provides a mathematical relationship between the concentrations of reactants and products at equilibrium
- Applies to any chemical reaction at equilibrium, regardless of the complexity or number of reactants and products involved
- The law of mass action is the basis for deriving the equilibrium constant expression for a given reaction

Reaction Quotient and Equilibrium

- The reaction quotient (Q) has the same mathematical form as the equilibrium constant expression but uses instantaneous concentrations instead of equilibrium concentrations
- Comparing Q to K helps determine the direction in which a reaction will proceed to reach equilibrium:
- If $Q < K$, the reaction will proceed in the forward direction (towards products) to reach equilibrium
- If $Q > K$, the reaction will proceed in the reverse direction (towards reactants) to reach equilibrium
- If $Q = K$, the reaction is at equilibrium, and no net change in concentrations occurs
- Monitoring the reaction quotient allows for predicting the direction of a reaction and determining when equilibrium is reached (when Q becomes equal to K)

Temperature Dependence of Equilibrium Constants

Effect of Temperature on Equilibrium

- Temperature changes affect the equilibrium constant and the position of equilibrium in a chemical reaction
- Increasing temperature favors the endothermic direction of a reaction, while decreasing temperature favors the exothermic direction
- The magnitude of the equilibrium constant changes with temperature, but the direction of change depends on whether the reaction is exothermic or endothermic
- For exothermic reactions, K decreases with increasing temperature, while for endothermic reactions, K increases with increasing temperature

Van 't Hoff Equation

- The van 't Hoff equation describes the relationship between the equilibrium constant and temperature:
$$\ln \frac{K_2}{K_1} = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$
- K_1 and K_2 are the equilibrium constants at temperatures T_1 and T_2 , respectively
- ΔH° is the standard enthalpy change of the reaction
- R is the universal gas constant (8.314 J/mol·K)
- The van 't Hoff equation allows for calculating the equilibrium constant at a different temperature, given the equilibrium constant at a known temperature and the standard enthalpy change of the reaction

Exothermic and Endothermic Reactions

- In exothermic reactions ($\Delta H^\circ < 0$), heat is released from the system to the surroundings
- Examples: combustion reactions, neutralization reactions (acid-base reactions)
- Increasing temperature shifts the equilibrium towards the reactants side, decreasing the equilibrium constant
- In endothermic reactions ($\Delta H^\circ > 0$), heat is absorbed by the system from the surroundings
- Examples: thermal decomposition of calcium carbonate (limestone), melting of ice
- Increasing temperature shifts the equilibrium towards the products side, increasing the equilibrium constant
- Understanding the temperature dependence of equilibrium constants is crucial for predicting the effect of temperature changes on the position of equilibrium and the yield of products in chemical reactions

Thermodynamic Basis of Equilibrium Constants

Relationship between Equilibrium Constant and Standard Gibbs Free Energy Change

- The equilibrium constant is related to the standard Gibbs free energy change (ΔG°) of a reaction by the following equation: $\Delta G^\circ = -RT \ln K$
- R is the universal gas constant (8.314 J/mol·K), and T is the absolute temperature in Kelvin
- The standard Gibbs free energy change represents the driving force for a chemical reaction at standard conditions (1 atm pressure, 298 K, and 1 M concentrations)
- A negative ΔG° indicates a spontaneous reaction (favoring products), while a positive ΔG° indicates a non-spontaneous reaction (favoring reactants)

Calculating Equilibrium Constants from Standard Gibbs Free Energy Change

- The equation relating ΔG° and K can be rearranged to solve for the equilibrium constant:
$$K = e^{-\Delta G^\circ / RT}$$
- By knowing the standard Gibbs free energy change of a reaction, the equilibrium constant can be calculated at a given temperature
- Conversely, if the equilibrium constant is known, the standard Gibbs free energy change can be determined using the same equation
- This relationship highlights the thermodynamic basis of equilibrium constants and provides a link between the thermodynamic favorability of a reaction and the concentrations of reactants and products at equilibrium

Factors Influencing Standard Gibbs Free Energy Change

- The standard Gibbs free energy change depends on the standard enthalpy change (ΔH°) and the standard entropy change (ΔS°) of a reaction: $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$
- ΔH° represents the heat absorbed or released by the reaction at constant pressure, while ΔS° represents the change in the system's disorder or randomness
- Reactions with a negative ΔH° (exothermic) and a positive ΔS° (increase in disorder) are more likely to have a negative ΔG° and thus be spontaneous and have a larger equilibrium constant
- Temperature affects the relative contributions of ΔH° and ΔS° to ΔG° , which in turn influences the equilibrium constant
- Understanding the thermodynamic basis of equilibrium constants allows for predicting the favorability of reactions and the magnitude of equilibrium constants based on the enthalpy and entropy changes of the system

12.3 Calculation of equilibrium compositions

Chemical reactions don't always go to completion. Equilibrium composition is when forward and reverse reaction rates balance out. This topic dives into calculating these compositions, a key skill for understanding real-world chemical processes.

We'll explore factors like temperature and pressure that influence equilibrium. We'll also learn about partial pressures, mole fractions, and iterative techniques for solving complex equilibrium problems. These tools are essential for predicting and controlling chemical reactions.

Reaction Equilibrium

Equilibrium State and Composition

- Equilibrium composition represents the concentrations or partial pressures of reactants and products at which the forward and reverse reaction rates are equal
- Stoichiometric coefficients in a balanced chemical equation determine the relative amounts of reactants consumed and products formed as the reaction proceeds towards equilibrium
- Extent of reaction (ξ) quantifies the progress of a reaction from the initial state to equilibrium
- Defined as the number of moles of a reactant consumed or a product formed divided by its stoichiometric coefficient
- Equilibrium yield measures the fraction of a limiting reactant that is converted to products at equilibrium
- Calculated as the ratio of the actual amount of product formed to the theoretical maximum amount based on the limiting reactant (ethanol production from glucose fermentation)

Factors Influencing Equilibrium

- Temperature changes affect the equilibrium composition by shifting the equilibrium position according to Le Chatelier's principle
- Increasing temperature favors the endothermic direction, while decreasing temperature favors the exothermic direction (Haber process for ammonia synthesis)
- Pressure changes influence the equilibrium composition for gaseous reactions where there is a change in the total number of moles between reactants and products
- Increasing pressure favors the side with fewer moles of gas, while decreasing pressure favors the side with more moles of gas (nitrogen dioxide dimerization)

Composition Measures

Partial Pressures and Mole Fractions

- Partial pressures represent the individual pressures exerted by each gas in a mixture, as if it occupied the entire volume alone
- Calculated using the ideal gas equation: $P_i = \frac{n_i RT}{V}$, where P_i is the partial pressure of gas i , n_i is the number of moles of gas i , R is the universal gas constant, T is the temperature, and V is the volume
- Mole fractions express the composition of a mixture as the ratio of the number of moles of each component to the total number of moles in the mixture
- Defined as $X_i = \frac{n_i}{n_{total}}$, where X_i is the mole fraction of component i , n_i is the number of moles of component i , and n_{total} is the total number of moles in the mixture

- Partial pressures and mole fractions are related by Dalton's law of partial pressures: $P_i = X_i P_{total}$, where P_{total} is the total pressure of the mixture (air composition: 78% nitrogen, 21% oxygen, 1% argon)

Calculation Methods

Iterative Techniques for Equilibrium Composition

- Iterative methods are used to solve for the equilibrium composition when the reaction involves multiple species and the equilibrium constants are known
- The basic steps involve assuming an initial composition, calculating the equilibrium constants using the assumed composition, comparing the calculated constants with the known values, and iteratively adjusting the composition until convergence is achieved
- Convergence is reached when the calculated equilibrium constants match the known values within a specified tolerance (water-gas shift reaction: $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$)
- Iterative techniques can be implemented using numerical methods such as the Newton-Raphson method or the bisection method
- These methods systematically refine the assumed composition by minimizing the difference between the calculated and known equilibrium constants (methanol synthesis from syngas: $\text{CO} + 2\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH}$)

12.4 Le Chatelier's principle and reaction yield

Le Chatelier's principle is a game-changer in chemical reactions. It explains how systems at equilibrium respond to changes, helping us predict and control reactions. This principle is key to understanding equilibrium shifts and optimizing reaction yields.

In this section, we'll explore how factors like concentration, temperature, and pressure affect equilibrium. We'll also dive into real-world applications, showing how industries use these principles to boost production efficiency.

Le Chatelier's Principle and Equilibrium Stress

Principles of Equilibrium Stress

- Le Chatelier's principle states that when a system at equilibrium is disturbed by a change in conditions, the system will shift to counteract the change and establish a new equilibrium
- Applies to all chemical equilibria, including reactions in solution, gas phase, and heterogeneous systems
- Provides a qualitative understanding of how equilibrium systems respond to external changes
- Helps predict the direction of equilibrium shift when conditions are altered

Types of Equilibrium Stress

- Stress on equilibrium refers to any change in conditions that disturbs the equilibrium state
- Common stresses include changes in concentration, temperature, pressure, and volume
- Adding or removing reactants or products (concentration changes) shifts the equilibrium position to consume the added species or replenish the removed ones

- Changing the temperature of an exothermic or endothermic reaction affects the equilibrium constant and causes a shift to favor the direction that absorbs or releases heat, respectively
- Altering the pressure or volume of a gaseous equilibrium system with unequal moles of reactants and products induces a shift to minimize the pressure change

Equilibrium Shift Response

- Equilibrium shift occurs in response to the applied stress to minimize its effect and re-establish equilibrium
- Direction of the shift depends on the nature of the stress and the reaction's characteristics (exothermic/endothermic, mole ratio of gaseous species)
- Shift proceeds until the forward and reverse reaction rates become equal again at the new equilibrium position
- Magnitude of the shift depends on the extent of the stress and the system's sensitivity to the changed condition (reaction quotient vs. equilibrium constant)

Factors Affecting Equilibrium

Concentration Effects

- Changing the concentration of reactants or products disturbs the equilibrium and induces a shift
- Adding reactants or removing products shifts the equilibrium to the right (towards products) to consume the excess reactants or replenish the removed products
- Removing reactants or adding products shifts the equilibrium to the left (towards reactants) to replenish the depleted reactants or consume the excess products
- Magnitude of the shift depends on the relative change in concentration and the reaction's stoichiometry
- Concentration changes do not affect the equilibrium constant, only the equilibrium position

Temperature Effects

- Temperature changes affect the equilibrium constant and cause a shift in the equilibrium position
- Increasing temperature in an endothermic reaction shifts the equilibrium to the right (towards products) to absorb the added heat
- Decreasing temperature in an endothermic reaction shifts the equilibrium to the left (towards reactants) to release heat
- Increasing temperature in an exothermic reaction shifts the equilibrium to the left (towards reactants) to reduce the heat released
- Decreasing temperature in an exothermic reaction shifts the equilibrium to the right (towards products) to increase the heat released
- Temperature changes alter the equilibrium constant by changing the reaction rates and the relative stability of reactants and products

Pressure and Volume Effects

- Pressure and volume changes affect gaseous equilibrium systems with unequal moles of reactants and products
- Increasing pressure (or decreasing volume) shifts the equilibrium towards the side with fewer moles of gas to minimize the pressure increase
- Decreasing pressure (or increasing volume) shifts the equilibrium towards the side with more moles of gas to counteract the pressure decrease
- Pressure and volume changes do not affect the equilibrium constant, only the equilibrium position
- Reactions with equal moles of gaseous reactants and products are not influenced by pressure or volume changes

Applications of Le Chatelier's Principle

Optimizing Reaction Yield

- Le Chatelier's principle can be applied to maximize the yield of desired products in equilibrium reactions
- Increasing the concentration of reactants, removing products, or adjusting temperature and pressure in favor of product formation shifts the equilibrium to the right and enhances the yield
- Continuously removing products (using selective membranes, distillation, or precipitation) drives the equilibrium towards product formation and improves the overall yield
- Choosing optimal reaction conditions (temperature, pressure) based on the reaction's characteristics (exothermic/endothermic, gas phase) maximizes the equilibrium constant and product yield

Industrial Applications

- Le Chatelier's principle is widely used in industrial processes to control reaction conditions and optimize product yield
- Haber-Bosch process for ammonia synthesis ($N_2 + 3H_2 \rightleftharpoons 2NH_3$) applies high pressure to shift the equilibrium towards ammonia formation
- Contact process for sulfuric acid production ($2SO_2 + O_2 \rightleftharpoons 2SO_3$) uses excess oxygen and removes SO_3 to drive the equilibrium forward
- Ostwald process for nitric acid synthesis ($4NH_3 + 5O_2 \rightleftharpoons 4NO + 6H_2O$; $2NO + O_2 \rightleftharpoons 2NO_2$; $3NO_2 + H_2O \rightleftharpoons 2HNO_3 + NO$) employs multiple equilibrium stages with optimized conditions for each step
- Industrial applications demonstrate the practical significance of Le Chatelier's principle in optimizing chemical processes and product yields

Unit 13 – Separation Processes in Thermodynamics

13.1 Distillation and absorption

Distillation and absorption are key separation processes in chemical engineering. They rely on differences in volatility or solubility to separate mixtures into their components. These methods are crucial for purifying products and recovering valuable materials in many industries.

Understanding the principles behind distillation and absorption is essential for designing efficient separation systems. We'll explore vapor-liquid equilibrium, mass transfer, and equipment design to grasp how these processes work and how to optimize them for various applications.

Distillation Fundamentals

Fractional Distillation Process

- Fractional distillation separates liquid mixtures into their component parts based on differences in boiling points
- Involves heating the mixture to vaporize components, then condensing and collecting them at different heights in a distillation column
- Repeated vaporization and condensation steps create a gradient of composition from bottom to top of the column
- More volatile components with lower boiling points are collected at the top, while less volatile, higher boiling point components are collected at the bottom (crude oil refining)

Vapor-Liquid Equilibrium Principles

- Raoult's law describes the vapor pressure of an ideal solution as proportional to the vapor pressure of each component and its mole fraction in the liquid phase
- $P_i = x_i P_i^*$, where P_i is the partial pressure of component i , x_i is its mole fraction in the liquid, and P_i^* is its vapor pressure as a pure component
- Relative volatility α_{ij} measures the ease of separating two components i and j based on their vapor pressure ratio: $\alpha_{ij} = \frac{y_i/x_i}{y_j/x_j}$
- Higher relative volatility indicates easier separation (ethanol-water $\alpha \approx 2$, benzene-toluene $\alpha \approx 2.5$)
- Theoretical plates represent the equilibrium stages in a distillation column where vapor and liquid phases are assumed to reach equilibrium
- More theoretical plates lead to better separation but increased column height and cost

Distillation Design and Analysis

McCabe-Thiele Graphical Method

- McCabe-Thiele method is a graphical approach to analyze and design distillation columns at constant pressure
- Plots equilibrium curve (vapor-liquid) and operating lines (rectifying and stripping sections) on an xy-diagram
- Stepping off stages between the operating lines determines the number of theoretical plates required
- Minimum reflux ratio can be found from the intersection of the q-line and equilibrium curve
- Optimum reflux ratio is typically 1.2 to 1.5 times the minimum reflux to balance separation and cost

Reflux Ratio Optimization

- Reflux ratio R is the ratio of liquid reflux L returned to the top of the column to the distillate product D withdrawn
- Higher reflux ratios improve separation but require larger columns and more energy input
- Total reflux ($R = \infty$) achieves maximum separation corresponding to the number of theoretical plates
- Optimizing reflux ratio balances product purity and recovery with capital and operating costs (typical values range from 1.1 to 5)

Absorption Fundamentals

Absorption Process Principles

- Absorption is a mass transfer operation where a soluble component is removed from a gas stream by dissolving it into a liquid solvent
- Absorption column contacts gas and liquid phases counter-currently to promote mass transfer
- Solute transfers from the gas phase to the liquid phase based on concentration gradients and solubility
- Henry's law relates the equilibrium partial pressure of a solute P_A to its liquid phase concentration C_A : $P_A = HC_A$, where H is Henry's constant

Mass Transfer and Separation Efficiency

- Mass transfer coefficient k_L quantifies the rate of solute transfer across the gas-liquid interface per concentration driving force
- Overall mass transfer is determined by gas and liquid side resistances: $\frac{1}{K_L} = \frac{1}{k_L} + \frac{H}{k_G}$
- Absorption factor $A = \frac{L}{mG}$ relates liquid L and gas G flow rates with slope of equilibrium line m
- Absorption efficiency depends on contact area, residence time, concentration driving forces, and solvent selection (water for ammonia, amines for acid gases)

Absorption Equipment

Packed Absorption Columns

- Packed columns are filled with packing materials that provide high interfacial area for gas-liquid contact
- Common packings include Raschig rings, Berl saddles, and structured sheet metal packings
- Packing characteristics like size, shape, surface area, and void fraction affect column performance
- Pressure drop and liquid holdup are key design considerations for packed columns (typically 3-8 theoretical stages)

Tray Absorption Columns

- Tray columns use a series of perforated plates or trays to create distinct stages for gas-liquid contact
- Liquid flows across each tray and down the column while gas bubbles up through the perforations
- Tray types include sieve, valve, and bubble-cap, each with different flow patterns and characteristics
- Tray spacing, weir height, and downcomer design affect tray efficiency and capacity (typically 5-15 theoretical stages)
- Tray columns can handle higher liquid rates and are less prone to maldistribution compared to packed columns

13.2 Extraction and leaching

Extraction and leaching are key separation techniques in thermodynamics. They involve transferring solutes between phases, like pulling caffeine from coffee beans or metals from ore. These methods are vital in industries from food to metallurgy.

Understanding extraction processes helps us grasp how molecules move between phases. We'll look at different setups, like cross-current and counter-current, and important factors like distribution coefficients and solvent choice. This knowledge is crucial for designing efficient separation systems.

Extraction Processes

Liquid-Liquid Extraction and Solid-Liquid Extraction

- Liquid-liquid extraction involves transferring a solute from one liquid phase to another immiscible or partially miscible liquid phase
- Commonly used in chemical processing, metallurgy, and nuclear reprocessing
- Relies on the difference in solubility of the solute between the two liquid phases (aqueous and organic solvents)
- Solid-liquid extraction involves the separation of a solute from a solid matrix using a liquid solvent
- The solvent dissolves the desired solute, leaving behind the insoluble solid residue
- Widely applied in the food industry for extracting oils, flavors, and bioactive compounds from plant materials (coffee, tea, spices)

Leaching and Soxhlet Extraction

- Leaching is a specific type of solid-liquid extraction where a solvent is used to extract a soluble component from a solid mixture
- The solvent percolates through the solid, dissolving the desired solute and leaving behind the insoluble residue
- Used in hydrometallurgy to extract metals from ores (copper, gold, uranium) and in the food industry to extract sugar from sugar beets or oil from seeds
- Soxhlet extraction is a continuous solid-liquid extraction method that uses a specialized apparatus to repeatedly extract a solute from a solid sample
- The solvent is heated, vaporized, and condensed, percolating through the solid sample in a thimble and extracting the solute
- Commonly used for extracting lipids from food samples and pesticides or pollutants from soil samples

Extraction Configurations

Cross-Current and Counter-Current Extraction

- Cross-current extraction involves contacting the solvent and the feed material in a single stage, with the solvent flowing perpendicular to the feed
- The solvent and feed are mixed, allowed to reach equilibrium, and then separated
- Simpler to operate but less efficient than counter-current extraction
- Counter-current extraction involves contacting the solvent and the feed material in multiple stages, with the solvent flowing in the opposite direction to the feed
- The most concentrated solvent contacts the most depleted feed, while the least concentrated solvent contacts the most concentrated feed
- Achieves a higher extraction efficiency and requires less solvent than cross-current extraction (used in liquid-liquid extraction columns and leaching processes)

Extraction Parameters

Distribution Coefficient and Partition Coefficient

- The distribution coefficient (K_D) is the ratio of the concentration of a solute in the extract phase to its concentration in the raffinate phase at equilibrium
- Represents the effectiveness of the extraction process and the affinity of the solute for the extract phase
- A higher K_D indicates a more favorable extraction, requiring fewer stages or less solvent to achieve the desired separation
- The partition coefficient (K_P) is similar to the distribution coefficient but specifically refers to the ratio of the solute concentration in two immiscible liquid phases at equilibrium
- Used in liquid-liquid extraction to describe the partitioning of the solute between the aqueous and organic phases

- Depends on factors such as temperature, pH, and the presence of other solutes or additives

Solvent Selection

- Solvent selection is crucial for optimizing extraction efficiency, selectivity, and downstream processing
- The solvent should have a high affinity for the desired solute, low affinity for unwanted components, and be immiscible with the feed phase
- Other factors to consider include solvent toxicity, flammability, environmental impact, and cost
- Common solvents used in extraction processes include:
 - Hydrocarbons (hexane, heptane) for extracting oils and lipids
 - Alcohols (ethanol, methanol) for extracting polar compounds and natural products
 - Chlorinated solvents (dichloromethane, chloroform) for extracting pesticides and pollutants
 - Supercritical fluids (carbon dioxide) for extracting high-value compounds with minimal solvent residues

13.3 Membrane separations

Membrane separations are a crucial part of many industrial processes, from water treatment to food production. These techniques use special barriers to separate molecules based on size, charge, or other properties, allowing for efficient purification and concentration of various substances.

Understanding membrane separations is key to grasping modern separation processes. We'll explore different types of membrane filtration, from reverse osmosis to pervaporation, and examine how factors like selectivity, flux, and concentration polarization affect their performance in real-world applications.

Membrane Filtration Processes

Pressure-Driven Membrane Processes

- Reverse osmosis applies high pressure to overcome osmotic pressure and force solvent through a semi-permeable membrane, retaining solute on the pressurized side (desalination of seawater)
- Ultrafiltration uses pressure to force liquid through a semi-permeable membrane with pore sizes from 0.01 to 0.1 micron, retaining macromolecules and colloids (protein concentration, wastewater treatment)
- Microfiltration employs membranes with pore sizes from 0.1 to 10 microns to separate suspended particles from a liquid under pressure (clarification of wine and beer, sterile filtration)
- Nanofiltration operates at lower pressures than reverse osmosis but higher than ultrafiltration, retaining molecules with sizes in the nanometer range (water softening, removal of pesticides and herbicides)

Concentration-Driven Membrane Process

- Pervaporation combines permeation and evaporation, using a dense non-porous membrane to separate liquid mixtures based on the preferential sorption and diffusion of one component (removal of volatile organic compounds from water, dehydration of organic solvents)

Membrane Performance Characteristics

Selectivity and Flux

- Membrane selectivity measures the ability of a membrane to separate components, often expressed as the ratio of permeabilities or concentrations of components in the permeate and feed streams
- Flux represents the volumetric flow rate of fluid passing through the membrane per unit area, influenced by pressure difference, concentration gradient, and membrane resistance

Concentration Polarization and Osmotic Pressure

- Concentration polarization occurs when retained solute accumulates near the membrane surface, forming a concentration gradient that reduces the effective driving force and limits flux (fouling of reverse osmosis membranes)
- Osmotic pressure arises from the difference in solute concentrations across a semi-permeable membrane, opposing the applied pressure and reducing the effective driving force in pressure-driven processes (limiting factor in high-salinity water desalination)

13.4 Adsorption and ion exchange

Adsorption and ion exchange are key separation techniques in fluid systems. These processes rely on the interaction between molecules and solid surfaces to remove specific components from mixtures.

Understanding adsorption isotherms, fixed-bed operations, and regeneration methods is crucial for designing efficient separation systems. These concepts help engineers optimize processes like water treatment, gas purification, and chemical separations.

Adsorption Isotherms and Materials

Adsorption Isotherms

- Adsorption isotherms describe the equilibrium relationship between the amount of adsorbate on the surface of an adsorbent and the pressure or concentration of the adsorbate in the gas or liquid phase at a constant temperature
- Commonly used to characterize the adsorption capacity and behavior of different adsorbent materials
- Provide insights into the interaction between the adsorbate and adsorbent surface, such as the strength of adsorption and the surface heterogeneity
- Two widely used adsorption isotherm models are the Langmuir isotherm and the Freundlich isotherm (activated carbon, zeolites)

Langmuir Isotherm

- Assumes monolayer adsorption on a homogeneous surface with a finite number of identical adsorption sites
- Adsorption occurs without interaction between adsorbed molecules, and each site can accommodate only one molecule
- Mathematically expressed as: $\frac{q}{q_m} = \frac{K_L C}{1 + K_L C}$, where q is the amount adsorbed per unit mass of adsorbent, q_m is the maximum adsorption capacity, K_L is the Langmuir constant, and C is the

equilibrium concentration of the adsorbate

- Applicable to systems with strong adsorbate-adsorbent interactions and limited multilayer adsorption (gases on solid surfaces, dyes on activated carbon)

Freundlich Isotherm

- Empirical model that describes adsorption on heterogeneous surfaces with a distribution of adsorption sites having different adsorption energies
- Assumes that the adsorption capacity increases with increasing adsorbate concentration, following a power-law relationship
- Mathematically expressed as: $q = K_F C^{1/n}$, where q is the amount adsorbed per unit mass of adsorbent, K_F and n are Freundlich constants, and C is the equilibrium concentration of the adsorbate
- Suitable for systems with multilayer adsorption and a wide range of adsorbate concentrations (organic compounds on activated carbon, heavy metals on zeolites)

Adsorbent Materials

- Activated carbon is a highly porous carbonaceous material with a large surface area (500-1500 m²/g) and a wide range of pore sizes
- Prepared by pyrolysis and activation of organic precursors (wood, coal, coconut shells) to create a network of micropores and mesopores
- Exhibits excellent adsorption capacity for a variety of organic compounds, gases, and heavy metals due to its high surface area and surface functional groups
- Zeolites are crystalline aluminosilicate materials with a uniform pore structure and high surface area (300-800 m²/g)
- Consist of a three-dimensional framework of SiO₄ and AlO₄ tetrahedra, forming channels and cavities of molecular dimensions
- Display selective adsorption properties based on the size and shape of their pores, making them useful for gas separation, catalysis, and ion exchange (molecular sieves, catalytic cracking)
- Ion exchange resins are synthetic polymeric materials with functional groups that can exchange ions with a solution
- Consist of a cross-linked polymer matrix (polystyrene, polyacrylate) with attached functional groups (sulfonic acid, quaternary ammonium)
- Used for the removal of ionic contaminants from aqueous solutions, such as water softening, demineralization, and wastewater treatment (softening of hard water, removal of heavy metals)

Fixed-Bed Adsorption and Regeneration

Fixed-Bed Adsorption

- Fixed-bed adsorption is a continuous process where a fluid (gas or liquid) containing the adsorbate is passed through a stationary bed of adsorbent particles
- As the fluid flows through the bed, the adsorbate is removed from the fluid and adsorbed onto the surface of the adsorbent

- The adsorption process continues until the adsorbent becomes saturated, and the concentration of the adsorbate in the effluent reaches a predetermined level (breakthrough)
- The performance of a fixed-bed adsorption system is characterized by the breakthrough curve, which represents the concentration of the adsorbate in the effluent as a function of time or the volume of fluid treated (activated carbon beds for gas purification, zeolite beds for water treatment)

Breakthrough Curve and Mass Transfer Zone

- The breakthrough curve is a plot of the ratio of the effluent concentration to the inlet concentration (C/C_0) versus time or the volume of fluid treated
- Initially, the effluent concentration is near zero, as the adsorbent effectively removes the adsorbate from the fluid
- As the adsorbent becomes saturated, the effluent concentration gradually increases until it reaches the breakthrough point ($C/C_0 = 0.05-0.10$)
- The mass transfer zone (MTZ) is the region of the bed where the adsorption process is actively occurring, and the concentration of the adsorbate changes from the inlet to the effluent level
- The MTZ moves through the bed as the adsorption progresses, and its width depends on factors such as the fluid velocity, adsorbent particle size, and mass transfer rates (adsorption of volatile organic compounds on activated carbon, removal of heavy metals by ion exchange resins)

Regeneration

- Once the adsorbent in a fixed-bed system becomes saturated, it needs to be regenerated to restore its adsorption capacity for subsequent adsorption cycles
- Regeneration can be achieved by various methods, depending on the nature of the adsorbate and the adsorbent
- Thermal regeneration involves heating the saturated adsorbent to a high temperature (200-500°C) to desorb the adsorbed species and regenerate the surface
- Chemical regeneration uses a regenerant solution (acids, bases, or salts) to displace the adsorbed species and regenerate the adsorbent
- Pressure swing adsorption (PSA) employs a reduction in pressure to desorb the adsorbed species, followed by repressurization for the next adsorption cycle
- Regeneration is a critical step in the adsorption process, as it determines the overall efficiency and economics of the system (regeneration of activated carbon by steam, regeneration of ion exchange resins by sodium chloride solution)

Unit 14 – Refrigeration and Liquefaction

14.1 Vapor compression cycle

The vapor compression cycle is the backbone of refrigeration systems. It uses a refrigerant to absorb heat from a cool space and reject it to a warmer environment, creating a cooling effect. This process involves four key components: evaporator, compressor, condenser, and expansion valve.

Understanding the vapor compression cycle is crucial for grasping refrigeration principles. It explains how refrigerants change states, absorb and release heat, and how system efficiency is measured. This knowledge is essential for designing, operating, and troubleshooting refrigeration systems in various applications.

Vapor Compression Cycle Components

Evaporator and Refrigerant

- Evaporator absorbs heat from the refrigerated space, causing the low-pressure, low-temperature refrigerant to evaporate
- Refrigerant enters the evaporator as a low-quality, two-phase mixture and leaves as a saturated or slightly superheated vapor
- Common types of evaporators include finned-tube, plate, and shell-and-tube heat exchangers (finned-tube evaporators in household refrigerators)

Compressor and Condenser

- Compressor increases the pressure and temperature of the refrigerant vapor, consuming work in the process
- Compressor types include reciprocating, scroll, and rotary compressors (scroll compressors in air conditioning systems)
- Condenser rejects heat from the high-pressure, high-temperature refrigerant to the surroundings, causing the refrigerant to condense
- Condenser designs include air-cooled, water-cooled, and evaporative condensers (air-cooled condensers in residential air conditioning units)

Expansion Valve

- Expansion valve reduces the pressure and temperature of the refrigerant, creating a low-pressure, low-temperature two-phase mixture
- Expansion devices include thermostatic expansion valves (TXVs), capillary tubes, and orifice plates (TXVs in larger refrigeration systems)
- TXVs regulate the refrigerant flow based on the evaporator outlet temperature, ensuring proper superheat

Performance Metrics

Coefficient of Performance (COP)

- COP measures the efficiency of a refrigeration system, defined as the ratio of the cooling capacity to the work input
- $COP = \frac{Q_{evap}}{W_{comp}}$, where Q_{evap} is the heat absorbed by the evaporator and W_{comp} is the work consumed by the compressor
- Higher COP values indicate more efficient refrigeration systems (typical COPs range from 2 to 4)

Pressure-Enthalpy Diagram

- Pressure-enthalpy (P-h) diagram graphically represents the thermodynamic states of the refrigerant throughout the vapor compression cycle
- P-h diagram includes lines of constant pressure, temperature, enthalpy, and quality
- Processes in the vapor compression cycle (evaporation, compression, condensation, and expansion) can be visualized on the P-h diagram
- P-h diagram helps in analyzing the performance, sizing components, and troubleshooting refrigeration systems

Refrigerant States

Subcooling

- Subcooling occurs when the refrigerant is cooled below its saturation temperature at a given pressure
- Subcooling ensures that the refrigerant enters the expansion valve as a liquid, preventing flash gas formation and improving system performance
- Degree of subcooling is the difference between the saturation temperature and the actual temperature of the refrigerant at the condenser outlet (typical subcooling ranges from 5 to 10°C)

Superheating

- Superheating occurs when the refrigerant is heated above its saturation temperature at a given pressure
- Superheating ensures that the refrigerant enters the compressor as a vapor, preventing liquid slugging and compressor damage
- Degree of superheat is the difference between the actual temperature and the saturation temperature of the refrigerant at the evaporator outlet (typical superheat ranges from 5 to 10°C)
- Superheat can be controlled by adjusting the expansion valve settings or using electronic expansion valves (EEVs)

14.2 Absorption refrigeration

Absorption refrigeration uses heat to power cooling, unlike traditional systems that use electricity. It's a clever way to create cold using warmth, making it great for places with extra heat lying around.

The system has some key parts: an absorber, generator, condenser, and evaporator. These work together with special fluid pairs to move heat and create cooling, all without a noisy compressor.

Components of Absorption Refrigeration

Main Components

- Absorber acts as a low-pressure vessel that absorbs the refrigerant vapor from the evaporator using a liquid absorbent solution
- Generator heats the refrigerant-absorbent solution to vaporize the refrigerant, which is then sent to the condenser
- Condenser cools and condenses the high-pressure refrigerant vapor into a liquid state, rejecting heat to the surroundings
- Evaporator allows the low-pressure liquid refrigerant to absorb heat from the space being cooled, causing it to evaporate into a vapor state

Additional Components

- Expansion valve reduces the pressure of the liquid refrigerant coming from the condenser before it enters the evaporator
- Solution pump circulates the refrigerant-absorbent solution between the absorber and the generator
- Heat exchanger improves system efficiency by preheating the refrigerant-absorbent solution entering the generator using the hot solution leaving the generator

Working Fluid Pairs

Characteristics of Working Fluid Pairs

- Working fluid pair consists of a refrigerant and an absorbent that have a strong affinity for each other
- Refrigerant should have a high enthalpy of vaporization to maximize cooling capacity (ammonia, water)
- Absorbent should have a strong ability to absorb the refrigerant vapor and be easily separated from the refrigerant when heated (water, lithium bromide)

Common Working Fluid Pairs

- Lithium bromide-water system uses water as the refrigerant and lithium bromide as the absorbent
- Operates under vacuum conditions due to the low vapor pressure of water
- Suitable for air-conditioning applications with chilled water temperatures above 0°C (32°F)
- Ammonia-water system uses ammonia as the refrigerant and water as the absorbent
- Operates at higher pressures compared to the lithium bromide-water system
- Suitable for refrigeration applications with evaporator temperatures below 0°C (32°F)

Performance Metrics

Coefficient of Performance (COP)

- Coefficient of Performance (COP) is the ratio of the cooling capacity provided by the system to the heat input required at the generator
- COP is a measure of the efficiency of the absorption refrigeration system
- Typical COP values for absorption refrigeration systems range from 0.6 to 1.2, depending on the working fluid pair and operating conditions

Heat-Driven Cycle Characteristics

- Absorption refrigeration is a heat-driven cycle that uses thermal energy (heat) as the primary input instead of mechanical work (compressors)
- Heat sources for absorption refrigeration can include waste heat, solar thermal energy, or natural gas combustion
- Absorption refrigeration systems are advantageous in situations where waste heat or low-cost thermal energy is readily available (combined heat and power plants, industrial processes)
- Heat-driven nature of the cycle makes absorption refrigeration systems more environmentally friendly compared to conventional vapor-compression systems that rely on electricity

14.3 Gas liquefaction processes

Gas liquefaction processes are crucial for storing and transporting gases efficiently. These methods cool gases below their boiling points, turning them into liquids. Understanding these processes is key to grasping the broader concepts of refrigeration and liquefaction.

The Linde and Claude cycles are fundamental liquefaction techniques. They use different expansion methods to cool gases, with the Claude cycle improving efficiency through an expansion turbine. Cascade and mixed refrigerant cycles offer even more advanced approaches for liquefying gases with low boiling points.

Liquefaction Cycles

Linde Cycle

- Simplest liquefaction cycle uses isenthalpic expansion through a throttling valve
- Compressed gas is cooled in a heat exchanger before expanding through the valve
- Expanded gas is partially liquefied and separated into liquid and vapor streams
- Vapor stream returns to the compressor through the heat exchanger to provide cooling

Claude Cycle

- Improves upon the Linde cycle by incorporating an expansion turbine
- A portion of the compressed gas expands through the turbine, generating work and reducing temperature

- Expanded gas from the turbine mixes with the throttled stream, increasing liquefaction efficiency
- Vapor stream returns to the compressor through multiple heat exchangers for improved cooling

Cascade and Mixed Refrigerant Cycles

- Cascade cycle uses multiple refrigerants with progressively lower boiling points
- Each stage provides cooling for the next stage's refrigerant
- Allows for efficient liquefaction of gases with low boiling points (helium, neon)
- Mixed refrigerant cycle employs a mixture of refrigerants with different boiling points
- Composition of the mixture is optimized for the specific gas being liquefied
- Provides a closer match to the cooling curve of the gas, improving efficiency

Joule-Thomson Effect

Joule-Thomson Expansion

- Isenthalpic expansion of a gas through a throttling valve or porous plug
- Temperature change during expansion depends on the Joule-Thomson coefficient (μ_{JT})
- $\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H$
- Positive μ_{JT} results in cooling, while negative μ_{JT} leads to heating

Inversion Temperature

- Temperature at which the Joule-Thomson coefficient changes sign
- Above the inversion temperature, expansion causes heating; below, it causes cooling
- Inversion temperature is unique for each gas and depends on pressure
- Gases must be below their inversion temperature for liquefaction using Joule-Thomson expansion

Expansion Turbine

- Alternative to Joule-Thomson expansion, generates work while reducing temperature
- Isentropic expansion process, more efficient than isenthalpic expansion
- Can be used to precool gases before Joule-Thomson expansion or as a standalone liquefaction step
- Allows for liquefaction of gases with high inversion temperatures (hydrogen)

Liquefaction Components

Heat Exchangers

- Critical components in liquefaction cycles, facilitate heat transfer between streams
- Countercurrent flow arrangement maximizes heat transfer efficiency
- Types of heat exchangers used in liquefaction:

- Plate-fin heat exchangers: Compact, high surface area, suitable for cryogenic temperatures
- Coil-wound heat exchangers: Flexible design, can handle high pressures
- Printed circuit heat exchangers: Highly compact, manufactured by etching channels into plates

Expansion Devices

- Throttling valves: Simple, reliable, and inexpensive; used for Joule-Thomson expansion
- Expansion turbines: More efficient than throttling valves, generate work while reducing temperature
- Radial turbines: Compact, high efficiency, suitable for small-scale liquefaction
- Axial turbines: Higher flow capacity, used in large-scale liquefaction plants

Liquefaction Efficiency

- Measure of the energy required to liquefy a unit mass of gas
- Expressed as the ratio of the minimum work required for liquefaction to the actual work consumed
- Factors affecting liquefaction efficiency:
 - Thermodynamic properties of the gas (boiling point, inversion temperature)
 - Efficiency of heat exchangers and expansion devices
 - Pressure levels and temperature differences in the cycle
- Improving liquefaction efficiency:
 - Optimizing heat exchanger design and minimizing temperature differences
 - Using multiple expansion stages or mixed refrigerant cycles
 - Recovering work from expansion turbines to offset compressor power consumption

14.4 Cryogenics and low-temperature behavior of fluids

Cryogenics explores the behavior of materials at extremely low temperatures, typically below -150°C . This field unlocks unique properties like superconductivity and superfluidity, which have applications in powerful magnets and efficient power transmission.

Cryogenic fluids, such as liquid helium and nitrogen, play crucial roles in cooling systems and research. Understanding their properties and handling techniques is essential for various applications, from medical imaging to quantum computing.

Cryogenic Phenomena

Extremely Low Temperature Behavior

- Cryogenic temperatures refer to extremely low temperatures, typically below -150°C or 123 K
- At these temperatures, materials exhibit unique properties and behaviors not observed at room temperature
- Examples of cryogenic temperatures include the boiling point of liquid nitrogen at -196°C (77 K) and liquid helium at -269°C (4 K)

- Superconductivity occurs in certain materials at cryogenic temperatures
- Electrical resistance drops to zero, allowing current to flow without energy loss
- Superconductors have applications in powerful electromagnets (MRI machines) and high-efficiency power transmission
- Superfluidity is a state of matter achieved by some fluids at cryogenic temperatures
- Superfluids flow without friction and have infinite thermal conductivity
- Liquid helium-4 becomes a superfluid below 2.17 K, while liquid helium-3 becomes a superfluid below 2.5 mK

Quantum Effects at Cryogenic Temperatures

- Quantum effects become more pronounced at cryogenic temperatures
- Particles exhibit wave-like properties and can tunnel through potential barriers
- Quantum computers operate at cryogenic temperatures to maintain the coherence of qubits
- Bose-Einstein condensates (BECs) form at temperatures close to absolute zero
- Atoms cool enough to occupy the lowest quantum state, behaving as a single entity
- BECs have applications in precision measurements, quantum simulations, and studying quantum phenomena

Cryogenic Fluids

Helium Liquefaction

- Helium liquefaction involves cooling helium gas to its liquefaction point of 4.2 K at atmospheric pressure
- The process requires multiple stages of compression, expansion, and heat exchange
- Liquid helium is used as a coolant for superconducting magnets, cryogenic research, and in medical imaging (MRI)
- Helium has two stable isotopes: helium-4 and helium-3
- Helium-4 is more abundant and has a higher boiling point (4.2 K) compared to helium-3 (3.2 K)
- Helium-3 is rare but has unique properties, such as forming a superfluid at lower temperatures than helium-4

Nitrogen Liquefaction

- Nitrogen liquefaction involves cooling nitrogen gas to its liquefaction point of 77 K at atmospheric pressure
- The process is simpler and less energy-intensive compared to helium liquefaction
- Liquid nitrogen is used for cryogenic storage, cooling, and in industrial processes (food freezing, cryotherapy)
- Liquid nitrogen has a higher boiling point and is less expensive than liquid helium

- It is often used as a pre-coolant for helium liquefaction systems
- Liquid nitrogen can cause rapid freezing and damage to living tissues due to its extremely low temperature

Cryogenic Equipment and Materials

Insulation and Storage

- Dewar flasks, also known as vacuum flasks, are used to store and transport cryogenic fluids
- They consist of double-walled containers with a vacuum between the walls to minimize heat transfer
- The inner container is made of materials with low thermal conductivity, such as stainless steel or borosilicate glass
- Thermal insulation is crucial for maintaining cryogenic temperatures and minimizing heat leaks
- Common insulation materials include multilayer insulation (MLI), aerogel, and vacuum insulation panels
- Proper insulation helps reduce boil-off losses and extends the storage time of cryogenic fluids

Low-Temperature Materials

- Materials used in cryogenic applications must maintain their properties at extremely low temperatures
- Metals such as stainless steel, aluminum, and copper are commonly used for their ductility and thermal conductivity
- Polymers, such as Teflon and Vespel, are used for their low thermal conductivity and resistance to thermal contraction
- Cryogenic seals and gaskets are designed to maintain tight seals at low temperatures
- Materials such as indium, lead, and Teflon are used for their malleability and ability to conform to surfaces
- Proper sealing is essential to prevent leaks and maintain the integrity of cryogenic systems

Unit 15 – Critical Phenomena in Supercritical Fluids

15.1 Critical point behavior and properties

Critical point behavior is crucial in understanding phase transitions and fluid properties. At the critical point, liquid and vapor phases become indistinguishable, leading to unique phenomena like critical opalescence and infinite compressibility.

Universality in critical phenomena reveals that diverse substances exhibit similar behavior near their critical points. This concept simplifies the study of critical behavior and has applications in various fields, from physics to materials science.

Critical Point Properties

Definition and Characteristics of the Critical Point

- Critical point represents the highest temperature and pressure at which a substance can exist in vapor-liquid equilibrium
- Occurs at the end of the vapor pressure curve where the properties of the liquid and vapor phases become identical
- Above the critical point, distinct liquid and vapor phases do not exist, and the substance becomes a supercritical fluid
- Critical point is characterized by the critical temperature (T_c), critical pressure (P_c), and critical density (ρ_c)

Critical Temperature, Pressure, and Density

- Critical temperature (T_c) is the highest temperature at which a substance can exhibit vapor-liquid equilibrium
- Above T_c , the substance exists as a single phase regardless of the applied pressure
- Example: The critical temperature of water is 647.1 K (373.9°C)
- Critical pressure (P_c) is the vapor pressure at the critical temperature
- Represents the highest pressure at which vapor-liquid equilibrium can occur
- Example: The critical pressure of water is 22.06 MPa
- Critical density (ρ_c) is the density of the substance at the critical point
- Corresponds to the average density of the coexisting liquid and vapor phases
- Example: The critical density of water is 322 kg/m³

Critical Isotherm and Its Significance

- Critical isotherm is the isotherm on a pressure-volume (P-V) diagram that passes through the critical point

- Represents the boundary between the vapor-liquid region and the supercritical region
- On the critical isotherm, the compressibility of the substance becomes infinite, and the distinction between liquid and vapor phases disappears
- The shape of the critical isotherm is characterized by a horizontal inflection point at the critical point

Phase Behavior Near the Critical Point

Phase Coexistence and Critical Opalescence

- Near the critical point, the properties of the coexisting liquid and vapor phases become more similar
- The density difference between the phases decreases, and the interfacial tension approaches zero
- Critical opalescence occurs near the critical point due to increased density fluctuations
- Causes the substance to appear cloudy or milky due to the scattering of light
- Example: Near the critical point, a transparent fluid may exhibit a bluish haze or opalescence

Compressibility and Density Fluctuations

- Compressibility, which is the change in volume with respect to pressure, diverges near the critical point
- The isothermal compressibility becomes infinite at the critical point, indicating large density fluctuations
- Density fluctuations near the critical point lead to the formation of local regions with higher or lower densities compared to the average density
- These density fluctuations contribute to the observed critical opalescence and the unique properties of the substance near the critical point

Universality of Critical Phenomena

Concept of Universality

- Universality refers to the observation that many substances exhibit similar behavior near their critical points, regardless of their specific chemical nature
- The critical exponents, which describe the power-law dependence of various properties near the critical point, are found to be universal for a wide range of substances
- Universality allows for the grouping of substances into universality classes based on their critical behavior
- Examples of universality classes include the Ising model, the Heisenberg model, and the XY model

Significance and Applications of Universality

- Universality simplifies the study of critical phenomena by reducing the number of independent variables needed to describe the system
- It allows for the development of generalized theories and models that can be applied to a wide range of substances

- Universality has implications in various fields, such as condensed matter physics, statistical mechanics, and materials science
- Understanding universality helps in predicting the behavior of substances near their critical points and in designing processes that exploit the unique properties of supercritical fluids (e.g., supercritical fluid extraction, supercritical fluid chromatography)

15.2 Supercritical fluid properties and applications

Supercritical fluids exist above a substance's critical temperature and pressure, combining liquid-like density with gas-like diffusivity. This unique state allows for high solubility, rapid mass transfer, and tunability, making them versatile solvents for various applications.

Supercritical fluids, especially CO₂, are used in extraction processes, offering advantages over traditional methods. They align with green chemistry principles, promoting sustainable and environmentally friendly industrial processes by reducing hazardous chemicals and minimizing waste.

Supercritical Fluid Properties

Unique Characteristics of Supercritical Fluids

- Supercritical fluids exist above the critical temperature and critical pressure of a substance
- Exhibit liquid-like density, allowing for high solubility and extraction efficiency
- Density can be up to 100 times greater than gases
- Possess gas-like diffusivity, enabling rapid mass transfer and penetration into porous materials
- Diffusivity is typically 100 times higher than liquids
- Lack a distinct liquid or gas phase, resulting in a single homogeneous phase

Solvent Power and Tunability

- Supercritical fluids have high solvent power, dissolving a wide range of compounds
- Solvent power is dependent on fluid density, which can be adjusted by changing temperature and pressure
- Tunability of supercritical fluids allows for selective extraction and separation processes
- Properties can be fine-tuned by manipulating temperature and pressure near the critical point
- Enables optimization of extraction conditions for specific target compounds
- Solvent power and tunability make supercritical fluids versatile solvents in various applications (pharmaceuticals, natural product extraction)

Applications of Supercritical Fluids

Supercritical Extraction Processes

- Supercritical extraction utilizes supercritical fluids to extract valuable compounds from materials
- Common applications include decaffeination of coffee and tea, extraction of essential oils and flavors
- Offers advantages over traditional extraction methods (liquid-liquid extraction, Soxhlet extraction)

- Higher efficiency, selectivity, and faster extraction times
- Eliminates the need for toxic organic solvents
- Supercritical CO₂ is widely used due to its low critical temperature (31.1°C), non-toxicity, and easy removal from extracted products

Green Chemistry and Sustainable Processes

- Supercritical fluids align with the principles of green chemistry, promoting sustainable and environmentally friendly processes
- Reduce the use of hazardous chemicals and solvents
- Minimize waste generation and energy consumption
- Supercritical CO₂ is considered a green solvent, as it is non-toxic, non-flammable, and readily available
- Can replace harmful organic solvents in various industrial processes (cleaning, dyeing, polymer processing)
- Supercritical fluid technology enables the development of cleaner and more efficient manufacturing processes (pharmaceuticals, food, materials)

15.3 Near-critical behavior and anomalies

Near-critical behavior is a wild ride in thermodynamics. As fluids approach their critical point, they start acting weird. Properties like compressibility and heat capacity go crazy, getting super big or even infinite!

This weirdness happens because of huge fluctuations in density and energy. These fluctuations spread out over long distances, making the fluid super sensitive to tiny changes. It's like the whole system becomes one big, connected blob!

Critical Phenomena and Fluctuations

Critical Fluctuations and Correlation Length

- Critical fluctuations are large-scale fluctuations in density and other properties that occur near the critical point
- These fluctuations become more pronounced and extend over larger distances as the critical point is approached
- Correlation length is a measure of the spatial extent of these fluctuations
- Near the critical point, the correlation length diverges, meaning it becomes very large (on the order of micrometers or even millimeters)
- This divergence indicates that the system becomes highly correlated over long distances, with fluctuations in one region affecting those in distant regions

Divergence and Critical Slowing Down

- Many thermodynamic properties exhibit divergent behavior near the critical point
- Divergence means that these properties tend toward infinity as the critical point is approached

- Examples of properties that diverge include compressibility, heat capacity, and thermal expansion coefficient
- Critical slowing down is another phenomenon observed near the critical point
- It refers to the slowing down of the system's response to perturbations or changes in external conditions
- Near the critical point, the system takes longer to relax back to equilibrium after a disturbance, as the fluctuations become more persistent and long-lived

Anomalous Properties Near Critical Point

Anomalous Compressibility

- Compressibility is a measure of how much a substance's volume changes in response to a change in pressure
- Near the critical point, the compressibility becomes anomalously large, meaning the substance becomes highly compressible
- This anomalous behavior is a consequence of the large-scale density fluctuations occurring near the critical point
- The divergence of compressibility near the critical point is related to the divergence of the correlation length
- Experimentally, this can be observed as a rapid change in density with small changes in pressure near the critical point

Anomalous Heat Capacity

- Heat capacity is a measure of the amount of heat required to change a substance's temperature by a certain amount
- Near the critical point, the heat capacity also exhibits anomalous behavior, becoming very large
- This means that a small addition of heat can cause a significant change in temperature near the critical point
- The anomalous heat capacity is related to the large-scale energy fluctuations occurring in the system
- Experimentally, this can be observed as a sharp peak in the heat capacity as a function of temperature near the critical point

Theoretical Approaches

Scaled Equations of State

- Scaled equations of state are theoretical models used to describe the behavior of fluids near the critical point
- These equations are based on the idea of scaling, which relates the behavior of a system at different scales (e.g., microscopic and macroscopic)
- Scaled equations of state take into account the universal features of critical phenomena, such as the divergence of correlation length and thermodynamic properties

- One example is the van der Waals equation, which can be rescaled to describe the behavior of fluids near the critical point
- These equations often involve scaling exponents, which characterize the power-law behavior of various properties near the critical point
- Scaled equations of state provide a framework for understanding and predicting the anomalous behavior of fluids in the critical region
- They have been successful in describing experimental data and have contributed to the development of a unified theory of critical phenomena

15.4 Phase transitions and critical exponents

Phase transitions and critical exponents are key concepts in understanding critical phenomena. They describe how systems change from one state to another and how physical properties behave near critical points.

These concepts are crucial for grasping the broader topic of critical phenomena and supercritical fluids. They explain why different systems can exhibit similar behavior near phase transitions, despite having different microscopic properties.

Critical Phenomena

Order Parameter and Critical Exponents

- Order parameter quantifies the degree of order in a system undergoing a phase transition
- Examples: magnetization in a ferromagnet, density difference between liquid and gas phases
- Critical exponents describe the behavior of physical quantities near the critical point
- Exponents characterize power-law dependencies of various quantities (order parameter, susceptibility, correlation length) as the system approaches the critical point
- Critical exponents are universal, meaning they are independent of the microscopic details of the system
- Depend only on the dimensionality of the system and the symmetry of the order parameter

Scaling Laws and Universality Classes

- Scaling laws relate the critical exponents to each other
- Derived from the assumption that the singular part of the free energy is a homogeneous function near the critical point
- Universality classes group systems with the same critical behavior, regardless of their specific microscopic interactions
- Systems within the same universality class share the same set of critical exponents
- Examples: Ising universality class (includes ferromagnets and liquid-gas systems), XY universality class (includes superfluids and superconductors)

Theoretical Approaches

Mean-Field Theory

- Mean-field theory is a simple approximation used to describe phase transitions
- Assumes that each particle interacts with an average (mean) field created by all other particles
- Neglects fluctuations and correlations between particles
- Provides qualitatively correct description of phase transitions but fails to predict correct critical exponents
- Examples: Curie-Weiss theory for ferromagnetism, van der Waals equation for liquid-gas transitions

Renormalization Group

- Renormalization group is a powerful method for studying critical phenomena
- Based on the idea of coarse-graining the system by successively averaging over small-scale fluctuations
- Renormalization group transformations relate the system at different length scales
- Fixed points of these transformations correspond to critical points
- Allows for the calculation of critical exponents and the understanding of universality
- Flow of the system under renormalization group transformations determines the universality class

Models and Phase Transitions

Ising Model

- Ising model is a simple lattice model used to study phase transitions
- Consists of discrete variables (spins) that can take two values (+1 or -1)
- Spins interact with their nearest neighbors through a coupling constant J
- Exhibits a phase transition from a disordered (paramagnetic) phase to an ordered (ferromagnetic) phase as temperature is lowered
- Critical temperature T_c depends on the lattice dimensionality and the coupling constant
- Exact solution is known in one and two dimensions
- Provides a benchmark for testing various approximation methods and numerical simulations

Continuous Phase Transitions

- Continuous phase transitions, also known as second-order phase transitions, are characterized by a continuous change in the order parameter across the critical point
- Examples: ferromagnetic transition, superfluid transition, superconducting transition
- At the critical point, the system exhibits scale invariance and long-range correlations
- Correlation length diverges, and the system becomes self-similar at all length scales

- Critical behavior is characterized by power-law dependencies and universal critical exponents
- Fluctuations and correlations dominate the behavior near the critical point, leading to the failure of mean-field theories