Chapter 11: Thermodynamics - Detailed Notes

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11.1 INTRODUCTION

Historical Context:

- **Early Concept**: Heat viewed as invisible fluid ("caloric") flowing from hot to cold bodies
- **Benjamin Thomson (Count Rumford, 1798)**: Revolutionary experiment showing heat as energy form
  - Boring brass cannon generated heat proportional to work done
  - Heat production independent of drill sharpness
  - Demonstrated work-to-heat conversion

Modern Understanding:

Thermodynamics: Branch of physics dealing with heat, temperature, and energy inter-conversion

Key Characteristics:

- **Macroscopic Science**: Deals with bulk properties, not molecular details
- **Few Variables**: Uses measurable quantities (P, V, T, mass, composition)
- **Historical Development**: Laws formulated before molecular theory was established

Thermodynamics vs Mechanics:

Aspect	Mechanics	Thermodynamics
Focus	Motion under forces	Internal macroscopic state

Aspect	Mechanics	Thermodynamics
Energy	Kinetic energy of whole system	Internal energy of constituents
Variables	Position, velocity	Pressure, volume, temperature

Practical Example:

- **Bullet fired**: Mechanical KE changes, not temperature
- **Bullet stops**: Mechanical KE → Heat, temperature increases

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11.2 THERMAL EQUILIBRIUM

Thermodynamic Equilibrium:

Definition: State where macroscopic variables don't change with time

Conditions for Equilibrium:

- Fixed values of pressure, volume, temperature
- Closed system, isolated from surroundings
- No changes in mass or composition over time

Wall Types:

Adiabatic Wall:

- **Property**: Prevents heat flow
- **Material**: Insulating wall
- **Result**: Any (P_1,V_1) compatible with any (P_2,V_2)

Diathermic Wall:

- **Property**: Allows heat flow
- **Material**: Conducting wall
- **Result**: System variables change until equilibrium achieved

Experimental Observation:

When adiabatic wall replaced by diathermic wall:

- Variables change: (P_A, V_A) → (P_A', V_A') and (P_B, V_B) → (P_B', V_B')
- **Final state**: Both systems in thermal equilibrium
- **Characteristic**: Equal temperatures in equilibrium

11.3 ZEROTH LAW OF THERMODYNAMICS

Statement:

"Two systems in thermal equilibrium with a third system separately are in thermal equilibrium with each other"

Experimental Setup:

1. **Stage 1**: Systems A and B separated by adiabatic wall, both in contact with system C via diathermic walls
2. **Stage 2**: A and B reach thermal equilibrium with C
3. **Stage 3**: Replace A-B adiabatic wall with diathermic wall, isolate C
4. **Observation**: No further change in A and B states

Mathematical Consequence:

> If T_A = T_C and T_B = T_C, then T_A = T_B

Physical Significance:

- **Establishes temperature concept**: Physical quantity equal for systems in thermal equilibrium
- **Foundation for thermometry**: Basis for temperature measurement
- **Transitive property**: Thermal equilibrium is transitive relation

Temperature Definition:

Temperature (T): Thermodynamic variable whose equality indicates thermal equilibrium

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11.4 HEAT, INTERNAL ENERGY AND WORK

Internal Energy (U):

Microscopic Definition:

Sum of kinetic and potential energies of all molecules in the system

Key Properties:

- **State Variable**: Depends only on current state, not history
- **Path Independent**: $U_2 - U_1$ same regardless of process path
- **Reference Frame**: Measured in frame where center of mass at rest
- **Excludes**: Kinetic energy of system as whole

Components:

- **Translational KE**: Linear motion of molecules
- **Rotational KE**: Rotation of molecules
- **Vibrational KE**: Vibration within molecules
- **Potential Energy**: Intermolecular interactions

Methods of Changing Internal Energy:

1. Heat Transfer (Q):

- **Mechanism**: Temperature difference between system and surroundings
- **Direction**: Hot → Cold
- **Process**: Energy in transit due to thermal contact

2. Work Transfer (W):

- **Mechanism**: Mechanical means (moving piston, compression, expansion)
- **Process**: Energy transfer without temperature difference
- **Examples**: Gas expansion, compression

Important Distinctions:

Heat vs Internal Energy:

- **Heat**: Energy in transit, not a state property
- **Internal Energy**: Energy contained in system, state property
- **Meaningless**: "Gas contains certain amount of heat"
- **Meaningful**: "Gas has certain internal energy" or "Heat supplied to gas"

Work in Thermodynamics:

- **Not a state variable**: Depends on process path

- **Energy transfer mode**: Mechanical energy exchange with surroundings

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11.5 FIRST LAW OF THERMODYNAMICS

Statement:

Energy supplied to system goes partly to increase internal energy and partly to do work on surroundings

Mathematical Expression:

$$\Delta Q = \Delta U + \Delta W$$

Where:

- **ΔQ**: Heat supplied to system (positive if absorbed)
- **ΔU**: Change in internal energy
- **ΔW**: Work done by system (positive if system does work)

Alternative Form:

$$\Delta Q - \Delta W = \Delta U$$

Physical Interpretation:

General law of energy conservation applied to thermodynamic systems

Path Dependence:

- **ΔU**: Path independent (state variable)
- **ΔQ, ΔW**: Generally path dependent

- **ΔQ - ΔW**: Always path independent (equals ΔU)

Special Case - Isothermal Process:

For ideal gas: ΔU = 0, therefore ΔQ = ΔW **All heat supplied converted to work**

Work by Gas Against Constant Pressure:

$$\Delta W = P\,\Delta V$$

Therefore: $\Delta Q = \Delta U + P\,\Delta V$

Practical Application:

Water → Steam transition:

- Latent heat: ΔQ = 2256 J/g
- Work done: ΔW = P(V_gas - V_liquid) = 169.2 J/g
- Internal energy change: ΔU = 2256 - 169.2 = 2086.8 J/g

Most energy goes to internal energy change

11.6 SPECIFIC HEAT CAPACITY

Heat Capacity (S):

$$S = \Delta Q/\Delta T$$

Specific Heat Capacity (s):

$$s = S/m = (1/m)(\Delta Q/\Delta T)$$

Units: J kg^{-1} K^{-1}

Molar Specific Heat Capacity (C):

$$C = (1/\mu)(\Delta Q/\Delta T)$$

Where μ = number of moles **Units**: J mol^{-1} K^{-1}

Properties:

- **Material dependent**: Different for different substances
- **Temperature dependent**: May vary with temperature
- **Process dependent**: Different values for different processes

Theoretical Prediction for Solids:

Using equipartition theorem:

$$U = 3RT \text{ (for one mole)}$$
$$C = \partial U/\partial T = 3R \approx 25 \text{ J mol}^{-1} \text{ K}^{-1}$$

Water Specific Heat:

- **Historical**: 1 calorie = heat to raise 1g water by 1°C
- **Precise definition**: 14.5°C to 15.5°C
- **SI value**: 4186 J kg^{-1} K^{-1}

- **Conversion**: 1 cal = 4.186 J

For Ideal Gas:

$$Cp - Cv = R$$

Where:

- **Cp**: Molar specific heat at constant pressure
- **Cv**: Molar specific heat at constant volume
- **R**: Universal gas constant

Derivation:

At constant volume: $Cv = \partial U/\partial T$ At constant pressure: $Cp = \partial U/\partial T + R$ Therefore: $Cp - Cv = R$

11.7 THERMODYNAMIC STATE VARIABLES AND EQUATION OF STATE

State Variables:

Macroscopic quantities that completely describe equilibrium state

Examples:

- Pressure (P)
- Volume (V)
- Temperature (T)
- Internal Energy (U)
- Mass (m)

Equilibrium vs Non-Equilibrium:

Equilibrium States:

- Well-defined state variables
- Uniform properties throughout system
- No change with time

Non-Equilibrium Examples:

- Free expansion into vacuum
- Explosive chemical reactions
- Rapid compression/expansion

Equation of State:

Relationship connecting state variables

Ideal Gas:

$$PV = \mu RT$$

Independence:

For μ fixed, only 2 variables independent (e.g., P and V determine T)

Classification of Variables:

Extensive Variables:

- **Property**: Proportional to system size
- **Examples**: Volume (V), Internal Energy (U), Total Mass (M)

- **Test**: Value halved when system divided in half

Intensive Variables:

- **Property**: Independent of system size
- **Examples**: Pressure (P), Temperature (T), Density (ρ)
- **Test**: Value unchanged when system divided in half

Consistency Check:

First Law: $\boxed{\Delta Q = \Delta U + P\Delta V}$

- Left side: Extensive (ΔQ)
- Right side: Extensive (ΔU) + Intensive × Extensive (PΔV) = Extensive **Dimensionally consistent**

11.8 THERMODYNAMIC PROCESSES

11.8.1 Quasi-Static Process

Definition:

Infinitely slow process where system remains in equilibrium with surroundings at every stage

Characteristics:

- System pressure ≈ External pressure (infinitesimal difference)
- System temperature ≈ Surroundings temperature
- **Reversible**: Can be turned back
- **Theoretical construct**: Real processes are approximations

Why Important:

- **Well-defined state variables**: At every instant
- **Calculable**: Can use equilibrium relations
- **Reversible**: Maximum efficiency possible

Special Processes:

Isothermal Process:

- **Condition**: T = constant
- **Example**: Gas expansion in large thermal reservoir
- **Ideal Gas**: PV = constant (Boyle's Law)

Isobaric Process:

- **Condition**: P = constant
- **Work done**: $W = P(V_2 - V_1)$

Isochoric Process:

- **Condition**: V = constant
- **Work done**: W = 0
- **Heat transfer**: All goes to internal energy change

Adiabatic Process:

- **Condition**: Q = 0 (thermally insulated)
- **Ideal Gas**: PV^{γ} = constant
- **Work-Energy**: $W = -\Delta U$

11.8.2 Isothermal Process

For Ideal Gas:

$$PV = \mu RT = \text{constant}$$

Work Done:

$$W = \int P\, dV = \mu RT \ln(V_2/V_1)$$

Energy Relations:

- **Internal energy**: $\Delta U = 0$ (temperature constant)
- **First Law**: $Q = W$
- **Heat absorbed**: Equals work done

11.8.3 Adiabatic Process

Ideal Gas Relation:

$$PV^{\gamma} = \text{constant}$$

Where $\gamma = Cp/Cv$

Work Done:

$$W = \mu R(T_1 - T_2)/(\gamma - 1)$$

Energy Relations:

- **Heat transfer**: Q = 0
- **First Law**: W = -ΔU
- **Work by gas**: Decreases internal energy

11.8.4 Isochoric Process

Characteristics:

- **Volume**: Constant
- **Work**: W = 0
- **Energy**: All heat goes to internal energy
- **Heat capacity**: Cv determines temperature change

11.8.5 Isobaric Process

Work Done:

$$W = P(V_2 - V_1) = \mu R(T_2 - T_1)$$

Energy Distribution:

- **Internal energy**: Changes due to temperature change
- **Work**: P ΔV
- **Heat capacity**: Cp determines temperature change

11.8.6 Cyclic Process

Definition:

Process where system returns to initial state

Properties:

- **Internal energy**: ΔU = 0 (state variable)
- **Net heat**: Q = W (net work done)
- **Applications**: Heat engines, refrigerators

11.9 SECOND LAW OF THERMODYNAMICS

Need for Second Law:

First Law alone insufficient to explain observed phenomena

Examples Forbidden by Second Law:

- Book jumping from table using thermal energy
- Heat flowing from cold to hot spontaneously
- 100% conversion of heat to work

Statements:

Kelvin-Planck Statement:

"No process is possible whose sole result is absorption of heat from reservoir and complete conversion into work"

Clausius Statement:

"No process is possible whose sole result is transfer of heat from colder to hotter object"

Physical Implications:

Heat Engines:

- **Efficiency**: $\eta < 1$ (never 100%)
- **Cannot**: Convert all heat input to work
- **Must**: Reject some heat to cold reservoir

Refrigerators:

- **COP**: Cannot be infinite
- **Cannot**: Move heat from cold to hot without work input
- **Must**: Consume energy to operate

Equivalence:

Both statements are completely equivalent - violation of one implies violation of the other

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11.10 REVERSIBLE AND IRREVERSIBLE PROCESSES

Reversible Process:

Process that can be exactly reversed, returning both system and surroundings to original states

Requirements:

- **Quasi-static**: Infinitely slow
- **No dissipation**: No friction, viscosity, etc.
- **Equilibrium**: System in equilibrium at every stage

Irreversible Process:

Process that cannot be exactly reversed

Examples:

- **Free expansion**: Gas expanding into vacuum
- **Heat conduction**: Temperature equalization
- **Friction**: Mechanical energy → heat
- **Diffusion**: Concentration equalization
- **Chemical reactions**: Combustion, etc.

Causes of Irreversibility:

1. **Non-equilibrium states**: Rapid processes
2. **Dissipative effects**: Friction, viscosity, resistance

Why Reversibility Matters:

- **Maximum efficiency**: Reversible engines most efficient
- **Theoretical limit**: Sets upper bound on performance
- **Practical comparison**: Real processes compared to reversible ideal

Practical Reality:

Irreversibility is the rule in nature - all real processes involve some irreversibility

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11.11 CARNOT ENGINE

Motivation:

What is maximum possible efficiency for heat engine operating between two thermal reservoirs?

Carnot Engine Requirements:

- **Reversible**: For maximum efficiency
- **Two reservoirs**: Hot (T_1) and cold (T_2)
- **Isothermal heat exchange**: To maintain reversibility
- **Adiabatic temperature change**: Only way to change temperature reversibly

Carnot Cycle Steps:

Step 1→2: Isothermal Expansion (T_1)

- **Process**: Heat Q_1 absorbed from hot reservoir
- **Work done**: $W_{1\to2} = \mu RT_1 \ln(V_2/V_1)$
- **Internal energy**: $\Delta U = 0$

Step 2→3: Adiabatic Expansion ($T_1 \to T_2$)

- **Process**: Temperature drops to T_2
- **Work done**: $W_{2\to3} = \mu R(T_1-T_2)/(\gamma-1)$
- **Heat**: $Q = 0$

Step 3→4: Isothermal Compression (T_2)

- **Process**: Heat Q_2 rejected to cold reservoir
- **Work done**: $W_{3\to4} = -\mu RT_2 \ln(V_3/V_4)$
- **Internal energy**: $\Delta U = 0$

Step 4→1: Adiabatic Compression ($T_2 \to T_1$)

- **Process**: Temperature rises to T_1
- **Work done**: $W_{4\to1} = -\mu R(T_1-T_2)/(\gamma-1)$

- **Heat**: $Q = 0$

Carnot Engine Efficiency:

Net Work:

$$W = Q_1 - Q_2$$

Efficiency:

$$\eta = W/Q_1 = 1 - Q_2/Q_1$$

Using adiabatic conditions:

For adiabatic processes: $V_2/V_3 = V_1/V_4$

Therefore: $\boxed{\eta = 1 - T_2/T_1}$

Universal Results:

Carnot's Theorem:

1. **No engine** can be more efficient than Carnot engine operating between same temperatures
2. **Efficiency independent** of working substance
3. **Universal relation**: $Q_1/T_1 = Q_2/T_2$ for any Carnot engine

Temperature Scale:

Carnot efficiency provides **truly universal thermodynamic temperature scale**

Proof of Maximum Efficiency:

Contradiction method: Assume more efficient engine exists

- Couple with Carnot refrigerator
- Net result: Heat extraction from cold reservoir with complete conversion to work
- **Violates Kelvin-Planck statement**
- Therefore: No engine can exceed Carnot efficiency

SUMMARY OF KEY FORMULAS

First Law:

$$\Delta Q = \Delta U + \Delta W$$

Specific Heat Relations:

$$s = (1/m)(\Delta Q/\Delta T)$$
$$C = (1/\mu)(\Delta Q/\Delta T)$$
$$C_p - C_v = R \text{ (ideal gas)}$$

Work in Different Processes:

- **General**: $W = \int P\, dV$
- **Isobaric**: $W = P\Delta V$
- **Isothermal**: $W = \mu RT \ln(V_2/V_1)$
- **Adiabatic**: $W = \mu R(T_1 - T_2)/(\gamma - 1)$

Process Relations:

- **Isothermal**: $PV = \text{constant}$
- **Adiabatic**: $PV^{\gamma} = \text{constant}$

- **Isobaric**: V/T = constant
- **Isochoric**: P/T = constant

Carnot Engine:

$\eta = 1 - T_2/T_1$
$Q_1/T_1 = Q_2/T_2$

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