THERMODYNAMICS: STUDY MATERIAL AND NUMERICAL PROBLEMS

1. CONCEPT OF SYSTEMS, SURROUNDINGS, AND STATE

System: The part of the universe under investigation.

Surroundings: Everything outside the system.

Boundary: The real or imaginary surface separating the system from its surroundings.

Types of Systems:

- **Open System:** Exchanges both energy and matter with its surroundings. (e.g., a pot of boiling water without a lid).
- **Closed System:** Exchanges energy but not matter with its surroundings. (e.g., a sealed flask of gas).
- **Isolated System:** Exchanges neither energy nor matter with its surroundings. (e.g., a perfectly insulated thermos flask).

State of a System: A set of conditions that completely describe the system. These are defined by state variables.

State Variables: Properties of the system that define its state. Examples include pressure (P), volume (V), temperature (T), and the amount of substance (n).

Intensive and Extensive Variables:

- **Intensive Variables:** Properties that do not depend on the size or amount of the system. They are independent of the mass. (e.g., temperature, pressure, density, concentration).
- **Extensive Variables:** Properties that depend on the size or amount of the system. They are dependent on the mass. (e.g., volume, mass, internal energy, enthalpy, entropy).

2. PARTIAL DERIVATIVES AND DIFFERENTIALS

Partial Derivatives: Used when a function depends on multiple variables. It represents the rate of change of the function with respect to one variable, holding all other variables constant.

For a function f(x, y), the partial derivative with respect to x is denoted as $(\partial f/\partial x)_y$.

Exact Differential: A differential whose integral depends only on the initial and final states, not on the path taken. For a function $z = f(x, y)$, $dz = M\,dx + N\,dy$ is an exact differential if $(\partial M/\partial y)_x = (\partial N/\partial x)_y$.

Inexact Differential: A differential whose integral depends on the path taken between the initial and final states. Heat (q) and work (w) are inexact differentials.

Path Function: A quantity whose value depends on the path taken between the initial and final states (e.g., heat and work).

State Function: A quantity whose value depends only on the initial and final states of the system, not on the path taken (e.g., internal energy, enthalpy, temperature, pressure, volume).

3. CONCEPT OF HEAT AND WORK

Heat (q): Energy transferred due to a temperature difference between the system and its surroundings.

Work (w): Energy transferred when a force acts over a distance. In thermodynamics, it often refers to expansion work (P-V work).

Sign Conventions (Commonly Used):

- Heat absorbed by the system: $q > 0$
- Heat released by the system: $q < 0$
- Work done by the system (expansion): $w < 0$
- Work done on the system (compression): $w > 0$

Note: Some texts use the opposite sign convention for work.

4. ZEROTH LAW OF THERMODYNAMICS

The Zeroth Law states that if two systems are each in thermal equilibrium with a third system, then they are in thermal equilibrium with each other. This law provides the basis for the concept of temperature.

5. THERMODYNAMIC REVERSIBILITY

Reversible Process: A process that can be reversed by an infinitesimal change in conditions, returning both the system and surroundings to their original states without any net change elsewhere. These processes are theoretical and occur infinitely slowly.

Irreversible Process: A process that cannot be reversed to restore the initial state of both the system and surroundings without leaving a permanent change in either. All real-world processes are irreversible.

6. INTERNAL ENERGY AND FIRST LAW OF THERMODYNAMICS

Internal Energy (U): The total energy contained within a system, including kinetic and potential energies of its molecules. It is a state function.

First Law of Thermodynamics: The law of conservation of energy. It states that the change in internal energy (ΔU) of a system is equal to the heat (q) added to the system plus the work (w) done on the system.

Mathematically: $\mathbf{\Delta U = q + w}$

For a process occurring at constant volume (isochoric), where no work of expansion is done ($w=0$), $\Delta U = q_v$.

7. ENTHALPY AND HEAT CAPACITY

Enthalpy (H): A thermodynamic property defined as $H = U + PV$. It is a state function. Enthalpy is particularly useful for processes occurring at constant pressure.

For a process at constant pressure ($\Delta P=0$), the heat transferred (q_p) is equal to the change in enthalpy (ΔH): $\mathbf{\Delta H = q_p}$

Heat Capacity (C): The amount of heat required to raise the temperature of a substance by one degree (Celsius or Kelvin).

Specific Heat Capacity (c): Heat capacity per unit mass (J/g·K or J/kg·K).

Molar Heat Capacity (C_m): Heat capacity per mole (J/mol·K).

<u>Relationships between C_p and C_v:</u>

C_p is the heat capacity at constant pressure, and C_v is the heat capacity at constant volume.

For an ideal gas, the relationship is:

$C_p - C_v = R$ (where R is the ideal gas constant)

This relationship arises because at constant pressure, some energy added as heat goes into doing expansion work (PΔV), whereas at constant volume, all added heat increases internal energy.

8. ISOTHERMAL AND ADIABATIC PROCESSES

Isothermal Process: A process that occurs at a constant temperature ($\Delta T = 0$).

For an ideal gas undergoing an isothermal process:

- $\Delta U = 0$ (since U depends only on T for an ideal gas)
- Therefore, from the First Law ($\Delta U = q + w$), we get $0 = q + w$, so **$q = -w$**. All heat exchanged is converted into work, or vice versa.
- Work done during an isothermal expansion (from V_1 to V_2) for an ideal gas is: **$w = -nRT \ln(V_2/V_1) = -nRT \ln(P_1/P_2)$**

Adiabatic Process: A process in which no heat is exchanged between the system and its surroundings ($q = 0$).

For an adiabatic process involving an ideal gas:

- From the First Law ($\Delta U = q + w$), we get **$\Delta U = w$**. All change in internal energy is due to work done.
- The relationship between P and V is given by **$PV^\gamma = \text{constant}$**, where γ (gamma) = C_p/C_v is the adiabatic index.
- The work done during an adiabatic process is: **$w = \Delta U = nC_v\Delta T = nC_v(T_2 - T_1)$**

9. CALCULATIONS INVOLVING IDEAL GASES IN DIFFERENT PROCESSES

For an ideal gas, $PV = nRT$.

Summary of Calculations for Ideal Gases:

Process Type	Condition	ΔU	ΔH	q	w	Relationship
Isothermal	$\Delta T = 0$	0	0	$-w$	$-nRT \ln(V_2/V_1)$	$PV = \text{constant}$
Adiabatic	$q = 0$	$nC_v\Delta T$	$nC_p\Delta T$	0	$nC_v\Delta T$	$PV^\gamma = \text{constant}$
Isochoric	$\Delta V = 0$	$nC_v\Delta T$	$nC_p\Delta T$	$nC_v\Delta T$	0	$P/T = \text{constant}$
Isobaric	$\Delta P = 0$	$nC_v\Delta T$	$nC_p\Delta T$	$nC_p\Delta T$	$-P\Delta V = -nR\Delta T$	$V/T = \text{constant}$

Key Constants for Ideal Gases:

- Ideal Gas Constant, $R \approx 8.314$ J/(mol·K) ≈ 0.0821 L·atm/(mol·K)
- $C_p - C_v = R$
- $\gamma = C_p/C_v$

10. THERMOCHEMISTRY: ENTHALPY OF REACTION, HESS'S LAW, ETC.

Enthalpy of Reaction (ΔH_{rxn}): The change in enthalpy that accompanies a chemical reaction under constant pressure.

Hess's Law of Constant Heat Summation: The total enthalpy change for a reaction is independent of the pathway taken; it depends only on the initial and final states. This means that if a reaction can be expressed as the sum of several steps, the enthalpy change for the overall reaction is the sum of the enthalpy changes for each step.

Enthalpy of Formation (ΔH_f°): The enthalpy change when one mole of a compound is formed from its constituent elements in their standard states under standard conditions (usually 298.15 K and 1 atm pressure).

Enthalpy of Combustion (ΔH_c°): The enthalpy change when one mole of a substance undergoes complete combustion with oxygen under standard conditions.

Calculations using Hess's Law:

$\Delta H_{rxn}^\circ = \Sigma$ (moles × ΔH_f° of products) - Σ (moles × ΔH_f° of reactants)

Kirchhoff's Equation: Relates the change in enthalpy of reaction (ΔH_{rxn}) to temperature, based on the heat capacities of reactants and products.

$d(\Delta H_{rxn})/dT = \Delta C_p$

Integrating this equation gives:

$\Delta H_{rxn}(T_2) = \Delta H_{rxn}(T_1) + \int_{T1}^{T2} \Delta C_p \, dT$

Where $\Delta C_p = \Sigma$ (moles × $C_{p,\ product}$) - Σ (moles × $C_{p,\ reactant}$).

NUMERICAL PROBLEMS AND SOLUTIONS

Problem 1: Isothermal Expansion

One mole of an ideal monatomic gas at 300 K is expanded isothermally from a volume of 10.0 L to 20.0 L. Calculate the work done by the gas and the heat absorbed by the gas.

Solution:

Given:

- $n = 1$ mol
- $T = 300$ K
- $V_1 = 10.0$ L
- $V_2 = 20.0$ L
- $R = 8.314$ J/(mol·K)

For an isothermal process, $\Delta U = 0$.

Work done (w) by the gas is given by: $w = -nRT \ln(V_2/V_1)$

$w = -(1 \text{ mol}) * (8.314 \text{ J/(mol·K)}) * (300 \text{ K}) * \ln(20.0 \text{ L} / 10.0 \text{ L})$

$w = -2494.2 \text{ J} * \ln(2)$

$w = -2494.2 \text{ J} * 0.6931$

$w \approx -1728.8 \text{ J}$

Since $\Delta U = q + w$ and $\Delta U = 0$, we have $q = -w$.

$q = -(-1728.8 \text{ J}) = 1728.8 \text{ J}$

Answer: The work done by the gas is approximately 1728.8 J, and the heat absorbed by the gas is approximately 1728.8 J.

Problem 2: Adiabatic Expansion

A sample of an ideal gas at 300 K expands adiabatically from a volume of 10.0 L to 20.0 L. If the adiabatic index (γ) for the gas is 1.4, calculate the final temperature and the work done by the gas.

Solution:

Given:

- $T_1 = 300$ K
- $V_1 = 10.0$ L
- $V_2 = 20.0$ L
- $\gamma = 1.4$
- Assume n = 1 mol (for calculation of work if needed, but T2 is independent of n)
- $R = 8.314$ J/(mol·K)

For an adiabatic process, $T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$

$T_2 = T_1 * (V_1/V_2)^{\gamma-1}$

$T_2 = 300 \text{ K} * (10.0 \text{ L} / 20.0 \text{ L})^{1.4-1}$

T_2 = 300 K * $(0.5)^{0.4}$

T_2 = 300 K * 0.7578

T_2 ≈ 227.3 K

Now, calculate the work done. For an adiabatic process, w = ΔU = $nC_v(T_2 - T_1)$.

We need C_v. For an ideal gas, $C_p - C_v = R$ and $\gamma = C_p/C_v$. So, $C_p = \gamma C_v$.

$\gamma C_v - C_v = R \Rightarrow C_v(\gamma - 1) = R \Rightarrow C_v = R / (\gamma - 1)$

C_v = 8.314 J/(mol·K) / (1.4 - 1) = 8.314 / 0.4 = 20.785 J/(mol·K)

Assuming n = 1 mol:

w = (1 mol) * (20.785 J/(mol·K)) * (227.3 K - 300 K)

w = 20.785 J/K * (-72.7 K)

w ≈ -1510.8 J

Answer: The final temperature is approximately 227.3 K, and the work done by the gas is approximately 1510.8 J (or -1510.8 J if work done *by* the system is positive).

Problem 3: Hess's Law

Calculate the standard enthalpy of formation of methane (CH_4) from the following data:

1. $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$ ΔH° = -890.3 kJ/mol
2. $C(graphite) + O_2(g) \rightarrow CO_2(g)$ ΔH° = -393.5 kJ/mol
3. $H_2(g) + ½O_2(g) \rightarrow H_2O(l)$ ΔH° = -285.8 kJ/mol

Solution:

We want to find ΔH_f° for $CH_4(g)$, which is the reaction:

$C(graphite) + 2H_2(g) \rightarrow CH_4(g)$

Using Hess's Law, we manipulate the given reactions:

- Reaction 2 provides CO_2: C(graphite) + O_2(g) → CO_2(g) ΔH° = -393.5 kJ/mol
- Reaction 3 provides H_2O. We need 2 moles of H_2O, so multiply Reaction 3 by 2:

  $2H_2$(g) + O_2(g) → $2H_2O$(l) ΔH° = 2 * (-285.8 kJ/mol) = -571.6 kJ/mol

- Reaction 1 is the combustion of CH_4. We need CH_4 as a product, so reverse Reaction 1:

  CO_2(g) + $2H_2O$(l) → CH_4(g) + $2O_2$(g) ΔH° = -(-890.3 kJ/mol) = +890.3 kJ/mol

Now, sum these modified reactions and their enthalpy changes:

C(graphite) + O_2(g) → CO_2(g) ΔH° = -393.5 kJ/mol

$2H_2$(g) + O_2(g) → $2H_2O$(l) ΔH° = -571.6 kJ/mol

CO_2(g) + $2H_2O$(l) → CH_4(g) + $2O_2$(g) ΔH° = +890.3 kJ/mol

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Sum: C(graphite) + $2H_2$(g) → CH_4(g)

Total ΔH° = (-393.5) + (-571.6) + (890.3) kJ/mol

Total ΔH° = -965.1 + 890.3 kJ/mol

Total ΔH° = -74.8 kJ/mol

Answer: The standard enthalpy of formation of methane is -74.8 kJ/mol.