Thermodynamics

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Thermodynamics and Thermochemistry

In this Session :

✓ Weightage of concepts
✓ Revision of Entire chapter
✓ Revising important formula
✓ Solving previous year questions with anticipated questions

Statistical Analysis

JEE Main		JEE Advanced
Average questions per year: 3-4 Marks weightage: 12-16 marks (out of 100) Consistency: Appears in every paper Question type distribution: Numerical Value: 40% Multiple Choice: 60%		Average questions per year: 2-3 Marks weightage: 8-12 marks (out of 66) Question type distribution: Integer Type: 35% Multiple Choice: 45% Matrix Match: 20%

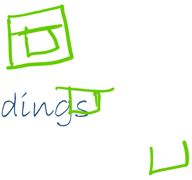
Most Tested Topics

First Law of Thermodynamics (25%)	Thermochemistry (20%)	Second Law & Entropy (18%)	State Functions (15%)	Rev./Irrev Processes (12%)	Heat Capacity & Kirchhoff's Law (10%)
Work calculations Internal energy changes Heat capacity relationships	Hess's Law applications Born-Haber cycle Enthalpy calculations	Spontaneity criteria Entropy changes Free energy calculations	Internal energy Enthalpy Gibbs free energy	Work calculations PV diagrams Maximum work principles	

Thermodynamics Notes for JEE

1. Types of Systems

Isolated System: No exchange of matter or heat with surroundings
Closed System: Only heat exchange possible, no matter exchange
Open System: Both matter and heat can be exchanged with surroundings



2. Key Properties

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Intensive Properties: Independent of quantity (temperature, pressure, viscosity)
Extensive Properties: Depend on quantity (mass, volume, entropy)
State Functions: Depend only on initial and final states (P, V, T)
Path Functions: Value depends on path followed

3. Laws of Thermodynamics

First Law:
Energy conservation principle: $\boxed{\overset{\text{energy}}{\Delta E} = \overset{\text{heat}}{q} + W} \rightarrow$ Work done.
Sign Conventions:
Work done on system (W): Positive
Work done by system (W): Negative
Heat absorbed (q): Positive
Heat released (q): Negative

$W = +ve$
$W = -ve$

Second Law
Heat cannot be completely converted to work without compensation
For spontaneous process: ΔG must be negative

$$\Delta S = \frac{q_{rev}}{T}$$

gas > liq > Solid

Third Law
Entropy of perfectly crystalline solids approaches zero at absolute zero

$$\lim_{T \to 0K} S \to 0$$

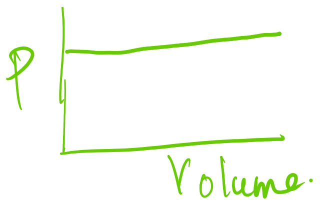
Free energy (G)

$$G = H - TS$$

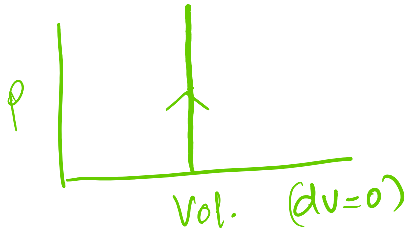
→ enthalpy

4. Important Processes

Isobaric Process ($\Delta P = 0$)
Constant pressure
Work done = $-P\Delta V$



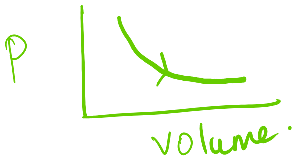
Isochoric Process ($\Delta V = 0$)
Constant volume
No work done



Isothermal Process ($\Delta T = 0$)
Constant temperature
For ideal gas: $W = -2.303nRT \log(V_2/V_1)$

$P\downarrow V\uparrow$

Adiabatic Process ($q = 0$) → heat
No heat exchange
PV^γ = constant
$TV^{\gamma-1}$ = constant

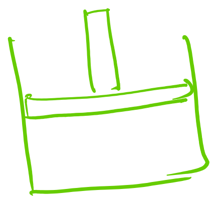


$dq = 0$

<u>Isothermal Expansion</u>
<u>Reversible Isothermal Expansion</u>

Isothermal Expansion

Reversible Isothermal Expansion



Exp $P \downarrow$ $V \uparrow$

Comp $P \uparrow$ $V \downarrow$

Work done:

$$w = -nRT \ln(V_2/V_1)$$
$$w = -nRT \ln(P_1/P_2)$$

Heat absorbed:

$$q = -w = nRT \ln(V_2/V_1)$$

Process is slow and controllable
Maximum work obtained

Irreversible Isothermal Expansion

Work done: X.

$$w = -P_{ext}(V_2 - V_1)$$

Less than reversible work

Heat absorbed:

$$q = -w$$

Rapid, uncontrolled process

Isothermal Compression

Work done by surroundings on system
Heat released to surroundings
For reversible process:

$$w = +nRT \ln(V_2/V_1) \quad +ve$$
$$q = -nRT \ln(V_2/V_1) \quad -ve$$

Adiabatic Expansion

Equations

Temperature relation:

$$\boxed{T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}} \quad X.$$

Pressure relation:

$$P_1V_1^{\gamma} = P_2V_2^{\gamma}$$

Work done:

$$w = C_v(T_1 - T_2)$$
$$w = [P_1V_1 - P_2V_2]/(\gamma-1)$$

Key Points

Temperature decreases during expansion
Internal energy decreases
System does work against surroundings
Final pressure lower than isothermal process

<u>Adiabatic Compression</u>
Equations
Same as expansion but:

Temperature increases ✓
Work done on system positive ✓
Internal energy increases ✓

Relationships

For compression:

$T_2 > T_1$

$P_2 > P_1$

$V_2 < V_1$

Work done:

$w = Cv(T_2 - T_1)$

5. Enthalpy (H)
Total heat content at constant pressure
$\Delta H = \Delta U + P\Delta V$ → Heat releases.
For exothermic reaction: $\Delta H < 0$ X.
For endothermic reaction: $\Delta H > 0$ → Heat absorbed.

6. Entropy (S)
Measure of randomness
Order: Gas > Liquid > Solid
$\Delta S = q_{rev}/T$
For reversible process: $\Delta S(\text{system}) + \Delta S(\text{surr}) = 0$

7. Free Energy (G)

$G = H - TS$
For spontaneous reaction: $\Delta G < 0$
At equilibrium: $\Delta G = 0$

8. Important Formulae for Calculations

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Joule: $1\ J = 4.184 \times 10^7$ ergs $= 4.2 \times 10^7$ ergs.

Work done: $W = F \times dx$

Heat capacity equation: $q = (w + m) \times c \times (T_2 - T_1)$

Clausius-Clapeyron equation (for liquid-vapor equilibrium):

$\log(P_2/P_1) = -\Delta H_v/2.303R \times (1/T_2 - 1/T_1)$

Q1. [JEE Advanced 2018]

A system absorbs 400J of heat and does 200J of work on the surroundings. Calculate: by the System

a) Change in internal energy of the system

b) Work done on the system

c) Heat released by the system

+200J

-400J

$$\Delta U = q + w$$
$$= 400 + (-200)$$
$$= +200J$$

$w = -ve$

$w = -200J$

Q2. [JEE Main 2019]

For an ideal gas undergoing isothermal expansion from 2L to 4L at 300K, calculate the entropy change. Given: n = 1 mol

$$\boxed{\Delta S = nR\ln\frac{V_2}{V_1}}$$
$$= (1)\ 8.314\ \ln\left(\frac{4}{2}\right)$$
$$= 5.76\ J/K$$

Q3. [JEE Advanced 2017]

A heat engine operates between 400K and 300K. Calculate:

a) Maximum theoretical efficiency

$$\eta = 1 - \frac{T_2}{T_1} = 1 - \frac{300}{400} = 0.25 \quad 25\%$$

b) Work output if heat input is 1000J at maximum efficiency

$Q = 1000J$

$Q = 1000 \, J$

$W = \eta Q = 0.25 \times 1000 = \underline{250 \, J}$

Q4. [JEE Advanced 2016]

For an adiabatic process, PV^1.4 = constant. If initial pressure and volume are 1 atm and 1L respectively, what is the final pressure when volume becomes 2L?

PV^{γ} $\boxed{\gamma = 1.4}$

$P_1 V_1^{\gamma} = P_2 V_2^{\gamma}$

$1 \times (1)^{1.4} = P_2 (2)^{1.4}$

$P_2 = \frac{(1)^{1.4}}{(2)^{1.4}}$

$= 0.379$ atm

$P_1 = 1 \, atm$ $P_2 = ?$

$V_1 = 1L$ $V_2 = 2L$

Q6. [JEE Main 2017]

A process has ΔH = 85 kJ and ΔS = 250 J/K. At what temperature will the process become spontaneous?

Ⓧ

$\Delta G = -ve$

$\Delta G = \Delta H - T\Delta S$

$0 = 85 \times 1000 - T(250)$

$T = \frac{8500\cancel{0}}{25\cancel{0}} = 340 \, K.$

Q7. [NEET 2019]

Calculate the work done in joules when 2 moles of an ideal gas expands isothermally and reversibly from 10L to 20L at 300K.

$$w = -nRT \ln\left(\frac{V_2}{V_1}\right)$$

$$= -2 \times 8.314 \times 300 \ln\left(\frac{20}{10}\right)$$

$$= -2 \times 8.314 \times 300 \ln(2)$$

$$= -3453\,J$$

Q8. [JEE Advanced 2015]

The entropy change for a reversible process in an isolated system is:

$$\Delta S_{(sys)} + \Delta S_{(surro)} = 0$$

$$\Delta S = 0$$

Q9. [JEE Main 2020]

Calculate the enthalpy change when 1 mole of water at 373K and 1 atm vaporizes.

Given: ΔH of vaporization = 40.7 kJ/mol

$$\Delta H = 40.7\ kJ/mol.$$

Q10. [NEET 2018]

A gas expands from 2L to 5L against a constant external pressure of 1 atm. Calculate the work done by the gas.

$\Delta P = 0.$ P

$$w = -P\Delta V$$

$w = -P\Delta V$

$= -(1)(5-2)$

$= -1(3) = -3\ L.atm$

$= -303.9\ J$

Q11. [JEE Advanced 2019]

Calculate the change in internal energy when 2 moles of an ideal monatomic gas is heated from 300K to 600K. Given: Cv = 3R/2

$\boxed{\Delta U = nC_v \Delta T}$

$\boxed{C_p - C_v = R}$

$= 2\left(\frac{3R}{2}\right)(300)$

$= 3 \times 8.314 \times 300$

$= 7482.6\ J$

Q12. [JEE Main 2016]

A process has ΔS = 100 J/K and ΔG = -10 kJ at 300K. Calculate ΔH.

ΔH

$\Delta G = \Delta H - T\Delta S$

$\Delta H = \Delta G + T\Delta S = -10 \times 1000 + 300 \times 100$

$= -10000 + 30000$

$= 20,000\ J$ (or)

$20\ kJ$.

Q13. [NEET 2021]

Calculate the maximum work that can be obtained from a heat engine operating between 400K and 300K if the heat absorbed at higher temperature is 1000J.

T

and 300K if the heat absorbed at higher temperature is 1000J.

$$\eta = 1 - \frac{T_2}{T_1}$$

$$= 1 - \frac{400}{300} = 0.25$$

$$W = \eta \times Q_1 = 0.25 \times 1000 = 250J$$

Q14. [JEE Advanced 2020]

For an ideal gas, calculate the work done during isothermal compression from 4L to 1L at 300K.

Given: n = 2 mol

✓

$$W = -nRT \ln \frac{V_2}{V_1}$$

Q15. [JEE Main 2018]

Calculate the entropy change when 1 mole of ice at 0°C melts to water at 0°C.

Given: Heat of fusion = 6.01 kJ/mol

$$\Delta S = \frac{\Delta H_{fusion}}{T}$$

$$= \frac{6.01 \times 1000}{273\,K} = 22.0\,J/K/mol.$$