

Thermodynamics

Thermodynamic terms

Intensive: These do not depend upon quantity of matter. e.g., T, P .

Extensive: These depend upon quantity of matter. e.g., mass, volume, energy.

Thermodynamic laws

Properties of system: Physical quantities which are used to define the system.

Thermodynamic processes

- If $dq = 0$, process is adiabatic.
- If $dT = 0$ and $dE = 0$, the process is isothermal.
- If $dV = 0$, process is isochoric.
- If $dP = 0$, process is isobaric.

Heat (q) and heat capacity (C)

- Heat capacity, $C = dq/dT$
- $C_v = \left(\frac{\partial U}{\partial T}\right)_V$; $C_p = \left(\frac{\partial H}{\partial T}\right)_P$
- When n_1 moles of gas A and n_2 moles of gas B are mixed.
$$(C_v)_{\text{mix}} = \frac{n_1 C_{v1} + n_2 C_{v2}}{n_1 + n_2}$$
- $C_p - C_v = nR$

Work (W)

- $W = -P_{\text{ext}} \Delta V$
[irreversible isothermal expansion]
- $W = -2.303nRT \log(P_1/P_2)$
- $W = -2.303nRT \log(V_2/V_1)$
[reversible isothermal expansion]
- $W = nC_v dT = \frac{nR}{\gamma - 1} (T_2 - T_1)$
[reversible adiabatic expansion]
where, $\gamma = C_p/C_v$
- $W = -P_{\text{ext}} R \left(\frac{T_2 P_1 - T_1 P_2}{P_1 P_2} \right)$
[irreversible adiabatic expansion]

Bond enthalpy
It is the enthalpy change accompanying the breaking of one mole of covalent bonds.
Bond enthalpy =
 \sum Bond enthalpies of reactants
 $- \sum$ Bond enthalpies of products

Enthalpy (H)
Total heat of the system

- $H = U + PV$
- $\Delta H = \Delta U + P\Delta V = C_p \Delta T = \Delta U + \Delta n_g RT$ (at constant pressure)
- $\Delta H = \sum H_{\text{product}} - \sum H_{\text{reactant}}$
= -ve (exothermic)
= +ve (endothermic)

Gibbs Free Energy (G)
Useful work done by the system

- $G = H - TS$
- $\Delta G = \Delta H - T\Delta S$
(Gibbs - Helmholtz equation)
$$\Delta G^\circ = \sum G_f^\circ(\text{product}) - \sum G_f^\circ(\text{reactant})$$
- $\Delta G^\circ = -2.303 RT \log K_{\text{eq}}$
- If $\Delta G = +ve$ (Non-spontaneous)
- If $\Delta G = -ve$ (Spontaneous)

Enthalpy of combustion, $\Delta_c H$
It is the enthalpy change when 1 mole of a substance burnt completely in air.

Hess's law of constant heat summation
 $\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$

Enthalpy change of a reaction
It is the enthalpy change when a given reactant reacts completely.

Enthalpy of formation
It is the enthalpy change occurring during the formation of 1 mole of a substance from its elements.

Enthalpy of solution
 $\Delta_{\text{sol}} H = \Delta_{\text{ionise}} H + \Delta H_{\text{hyd}}$
where, $\Delta_{\text{ionise}} H = S + I + \frac{1}{2} D - \Delta_f H + E.A.$

Zeroth law: System in thermal equilibrium with each other have same temperature.

First law: The total energy of the universe remains constant although it may undergo transformation from one form to the other.
 $\Delta U = q + w$ ($\Delta U =$ internal energy)

Second law: In a spontaneous process total energy of the universe increases.
 $\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}} > 0$

Entropy (S)
Measure of randomness or disorder

- $\Delta S = \frac{q_{\text{rev}}}{T}$ (reversible process)
- $\Delta S = 2.303n C_v \log\left(\frac{T_2}{T_1}\right) + 2.303nR \log\left(\frac{V_2}{V_1}\right)$
- $\Delta S = 2.303n C_p \log\left(\frac{T_2}{T_1}\right) + 2.303nR \log\left(\frac{P_1}{P_2}\right)$
- $\Delta S = 2.303nR \log\left(\frac{V_2}{V_1}\right)$ } isothermal
- $\Delta S = 2.303nR \log\left(\frac{P_1}{P_2}\right)$ }
- $\Delta S = 2.303n C_p \log\left(\frac{T_2}{T_1}\right)$ [isobaric]

Third law

- Entropy of all pure crystals is zero at the absolute zero temperature.
- $\lim_{T \rightarrow 0} S = 0$
- Residual Entropy
 $S_R = k \ln W$
($W =$ thermodynamic probability)

Thermodynamics Mechanical Engineering Notes

Daniel F McAuley



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Table of Contents Thermodynamics Mechanical Engineering Notes

1. Understanding the eBook Thermodynamics Mechanical Engineering Notes
 - The Rise of Digital Reading Thermodynamics Mechanical Engineering Notes
 - Advantages of eBooks Over Traditional Books
2. Identifying Thermodynamics Mechanical Engineering Notes
 - Exploring Different Genres
 - Considering Fiction vs. Non-Fiction
 - Determining Your Reading Goals
3. Choosing the Right eBook Platform
 - Popular eBook Platforms
 - Features to Look for in an Thermodynamics Mechanical Engineering Notes
 - User-Friendly Interface
4. Exploring eBook Recommendations from Thermodynamics Mechanical Engineering Notes

- Personalized Recommendations
 - Thermodynamics Mechanical Engineering Notes User Reviews and Ratings
 - Thermodynamics Mechanical Engineering Notes and Bestseller Lists
5. Accessing Thermodynamics Mechanical Engineering Notes Free and Paid eBooks
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 - Thermodynamics Mechanical Engineering Notes Compatibility with Devices
 - Thermodynamics Mechanical Engineering Notes Enhanced eBook Features
 7. Enhancing Your Reading Experience
 - Adjustable Fonts and Text Sizes of Thermodynamics Mechanical Engineering Notes
 - Highlighting and Note-Taking Thermodynamics Mechanical Engineering Notes
 - Interactive Elements Thermodynamics Mechanical Engineering Notes
 8. Staying Engaged with Thermodynamics Mechanical Engineering Notes
 - Joining Online Reading Communities
 - Participating in Virtual Book Clubs
 - Following Authors and Publishers Thermodynamics Mechanical Engineering Notes
 9. Balancing eBooks and Physical Books Thermodynamics Mechanical Engineering Notes
 - Benefits of a Digital Library
 - Creating a Diverse Reading Collection Thermodynamics Mechanical Engineering Notes
 10. Overcoming Reading Challenges
 - Dealing with Digital Eye Strain
 - Minimizing Distractions
 - Managing Screen Time
 11. Cultivating a Reading Routine Thermodynamics Mechanical Engineering Notes
 - Setting Reading Goals Thermodynamics Mechanical Engineering Notes
 - Carving Out Dedicated Reading Time
 12. Sourcing Reliable Information of Thermodynamics Mechanical Engineering Notes

- Fact-Checking eBook Content of Thermodynamics Mechanical Engineering Notes
 - Distinguishing Credible Sources
13. Promoting Lifelong Learning
- Utilizing eBooks for Skill Development
 - Exploring Educational eBooks
14. Embracing eBook Trends
- Integration of Multimedia Elements
 - Interactive and Gamified eBooks

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