

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

J. Patterson



Thermodynamics Mechanical Engineering Notes:

Lecture Notes for Thermodynamics for Engineers and Chemists Massachusetts Institute of Technology. Department of Mechanical Engineering, Massachusetts Institute of Technology. Special Summer Program on Thermodynamics for Engineers and Chemists, 1958, 1958* *Thermodynamics and Energy Conversion* Henning Struchtrup, 2014-07-02 This textbook gives a thorough treatment of engineering thermodynamics with applications to classical and modern energy conversion devices Some emphasis lies on the description of irreversible processes such as friction heat transfer and mixing and the evaluation of the related work losses Better use of resources requires high efficiencies therefore the reduction of irreversible losses should be seen as one of the main goals of a thermal engineer This book provides the necessary tools Topics include car and aircraft engines including Otto Diesel and Atkinson cycles by pass turbofan engines ramjet and scramjet steam and gas power plants including advanced regenerative systems solar tower and compressed air energy storage mixing and separation including reverse osmosis osmotic power plants and carbon sequestration phase equilibrium and chemical equilibrium distillation chemical reactors combustion processes and fuel cells the microscopic definition of entropy The book includes about 300 end of chapter problems for homework assignments and exams The material presented suffices for two or three full term courses on thermodynamics and energy conversion

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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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