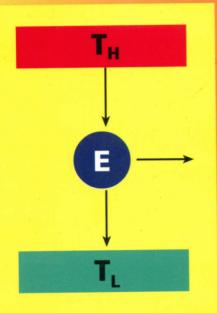
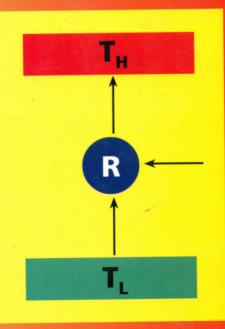
# THRMODYNAMICS







# CONTENTS

#### Preface Nomenclature

#### **1** INTRODUCTION

- 1.1 Initiation 1
- 1.2 Energy Sources 2
- 1.3 Two Categories of Thermal Plants 2
- 1.4 Examples of Work Producing and Work Consuming Plants 3
- 1.5 Indirect and Direct Energy Conversion 3
- 1.6 Nomenclature for Heat and Work 4
- 1.7 Thermal Efficiency and Coefficient of Performance 4
- 1.8 External Combustion versus Internal Combustion 5
- 1.9 Some Common Thermodynamic Applications 6
- 1.10 Heat and Work Interactions of Heat Engines and Refrigerators 11
- 1.11 Concluding Remarks 13 Problems 13

#### 2 THERMODYNAMIC CONCEPTS AND THE ZEROTH LAW

- 2.1 Thermodynamic System: The Control Mass (Closed system) and the Control Volume (Open System) 15
- 2.2 Macroscopic versus Microscopic Point of View 17
- 2.3 The Working Substance 18
- 2.4 The Pure Substance 18
- 2.5 Thermodynamic Properties 18
- 2.6 Properties of a System and Thermodynamic Equilibrium 21
- 2.7 Thermodynamic Process 23
- 2.8 Thermodynamic Cycles 26
- 2.9 Fundamental Units 26

15

vii

xix

- 2.10 Specific Volume and Density 27
- 2.11 Units of Force/Weight 28
- 2.12 Pressure and Its Units 30
- 2.13 Concept of Temperature 34
- 2.14 Zeroth Law of Thermodynamics 36
- 2.15 Empirical Temperature Scales 40
- 2.16 Concept of Ideal or Perfect Gas 44
- 2.17 Perfect Gas Thermometer 44
- 2.18 Ideal Gas or Perfect Gas Temperature Scale 46
- 2.19 The International Practical Temperature Scale 48
- 2.20 Comparison of Thermometers 50 Problems 51

#### **3 PROPERTIES OF A PURE SUBSTANCE**

- 3.1 Phase Equilibrium of a Pure Substance on T-v Diagram 55
- 3.2 Thermodynamic Surfaces 66
- 3.3 p-v Diagram of a Pure Substance 68
- 3.4  $p_{sat}$  versus  $T_{sat}$  Phase Diagram of a Pure Substance 72
- 3.5 Independent Properties of a Pure Substance 74
- 3.6 Tables of Thermodynamic Properties 74
- 3.7 The Gaseous Phase: Equation of State 80
- 3.8 Ideal or Perfect Gas 80
- 3.9 Kinetic Theory of Gases and van der Waals Equation of State 85
- 3.10 Other Equations of State 86
- 3.11 Real Gas: Compressibility 88
- 3.12 Conditions of Critical Isotherm 91
- 3.13 Virial Equations of State 93
- 3.14 The Cubic Equation of State 95
- 3.15 Redlich-Kwong (R-K) Equation of State and Its Solution 96 Problems 99

#### 4 WORK AND HEAT

- 4.1 Energy and Its Forms 105
- 4.2 Thermodynamic Work 106
- 4.3 Units of Work, Power and Energy 107
- 4.4 Work Done in a Frictionless Quasi-Equilibrium Process in a Compressible System 109
- 4.5 Work Done in an Irreversible Process 117
- 4.6 Illustrations of Two Inherently Irreversible Processes 122
- 4.7 Flow Work 124
- 4.8 Nonflow Process versus Flow Process 124
- 4.9 Reciprocating Compressors 130 second proceeding
- 4.10 Work Done in a Machine Cycle 133

- 139 Indicator Diagram of a Reciprocating Machine 4.11 ties bui
- 4.12 Other Modes of Work Transfer 143
- 4.13 The State Postulate 145
- 4.14 Heat 145

5

- 148 Modes of Heat Transfer 4.15
- 4.16 Electrical Analogy 153
- Overall Hear Transfer Coefficient 154 4.17 Problems 157

#### FIRST LAW OF THERMODYNAMICS AND INTERNAL ENERGY AND ENTHALPY

164

- Joule's Experiment 164 5.1
- 5.2 First Law of Thermodynamics for a System Undergoing a Thermodynamic Cycle 166
- 5.3 First Law of Thermodynamics for a Process in a Closed System 169
- 5.4 The Thermodynamic Property—Internal Energy 171
- 5.5 The Thermodynamic Property—Enthalpy 176
- First Law Equation for a Reversible Process 178 5.6
- 5.7 Heart Transfer—Sensible and Latent 179
- Pressure—Enthalpy Diagram 5.8 183
- Calculation of Internal Energy and Enthalpy of a 5.9 Pure Substance 183
- Internal Energy and Enthalpy of an Ideal Gas 185 5.10
- Application of the First Law to Nonflow Processes 189 5.11
- 5.12 First Law as-a Rate Equation 197
- 5.13 First Law of Thermodynamics for a Process in an Open System 197
  - Steady-State Steady-Flow Energy Equation 201 5.14
  - Expressions from First Law for Work Done in 5.15 Nonflow and Flow Processes 202
  - Thermodynamics of Fluid Flow 203 5.16
  - 204 Steady Flow of a Fluid with Work Interaction 5.17
  - 5.18 Steady Flow of a Fluid with Area Changes 208
  - 5.19 Some More SSSF Processes 215
  - Unsteady-State Analysis 220 5.20 Problems 221

#### SECOND LAW OF THERMODYNAMICS AND ENTROPY 6

- Basis for Second Law 231 6.1
- 6.2 Direction or Spontaniety of Processes 233
- 6.3 Impossibility of Certain Thermodynamic Cycles 233
- Illustrations of Actual Heat Engines 235 6.4
- Kelvin-Planck Statement of the Second Law of 6.5 Thermodynamics 236

- 6.6 Illustration of an Actual Refrigerator/Heat Pump 238
- 6.7 Clausius Statement of the Second Law of Thermodynamics 239
- 6.8 Equivalence of Kelvin–Planck and Clausius Statements 241
- 6.9 Ideal Process 243
- 6.10 Factors That Make Processes Irreversible 244
- 6.11 Reversible Heat Transfer Process 247
- 6.12 Characteristics of Reversible and Irreversible Processes 248
- 6.13 The Carnot Cycle 249
- 6.14 The Carnot Principle 252
- 6.15 Thermodynamic or the Absolute Temperature Scale 255
- 6.16 Clausius Inequality 264
- 6.17 Second Law for a Thermodynamic Process in a Closed System 266
- 6.18 Temperature—Entropy Diagram 271
- 6.19 The Two T dS Equations 273
- 6.20 Entropy Change of an Ideal Gas 278
- 6.21 Entropy Production or Entropy Generation in a Closed System 287
- 6.22 Principle of Increase of Entropy for a Closed System and Surroundings (Universe) 288
- 6.23 Second Law of Thermodynamics for a Process in an Open System 295
- 6.24 Combined First and Second Law Formulation for Processes 305 Problems 306

#### 7 COMBINED FIRST AND SECOND LAWS APPLICATION TO PROCESSES

314

- 7.1 Problem Analysis and Solution Procedure 314
- 7.2 Nonflow Processes 315
- 7.3 Flow Processes 326
- 7.4 Velocity of Sound in a Fluid 327
- 7.5 Stagnation State 330
- 7.6 Flow Through a Turbine 332
- 7.7 Flow Through a Compressor 336
- 7.8 Reversible Adiabatic Flow of a Fluid with Area Change 341
- 7.9 Flow Through a Nozzle 342
- 7.10 Flow Through a Diffuser 345
- 7.11 Throttling Process 351
- 7.12 Separating and Throttling Calorimeter 352 Problems 354

#### 8 VAPOUR CYCLES

8.1 Classification of Cycles 358

- 8.2 Vapour Power Cycles 361
- Carnot Vapour Power Cycle 361 8.3
- Simple Rankine Cycle 364 8.4
- Effect of Internal Irreversibilities on Actual 8.5 Cycle Efficiencies 369
- Effect of Design and Operating Conditions in Rankine Cycle 373 8.6
- The Reheat Cycle 378 8.7
- 8.8 The Regenerative Principle 381
- Ideal Regenerative Cycle 381 8.9
- Overall Efficiency of a Steam Power Plant 388 8.10
- Supercritical Rankine Cycle 390 8.11
- Combined Heat and Power (CHP) or Cogeneration 391 8 12
- Vapour Refrigeration Cycles 392 813
- Reversed Carnot Vapour Cycle 393 8.14
- Limitations of Reversed Carnot Vapour Cycle 395 8.15
- Vapour Compression Cycle 397 8.16
- Vapour Absorption System 404 8.17 Problems 406

#### GAS CYCLES 9

- Internal Combustion Engines 411 9.1
- Important Parameters in Internal Combustion Engine 9.2 Cycles 418
- Air-Standard Cycles 420 9.3
- Air-Standard Cycles for Reciprocating I.C. Engines 421 9.4 IN BROGE V EL
- 9.5 Supercharging 433
- Air Standard Cycles for Gas Turbine Engines/Plants 435 9.6
- 9.7 Combined Cycle 448
- 9.8 Aircraft and Jet Propulsion Engines 450
- Gas Cycle Refrigeration 455 9.9
- 9.10 Cycles with Carnot Efficiency 462 Problems 464

#### AVAILABILITY AND IRREVERSIBILITY 10 Partial Property 17

- Quality of Energy 469 10.1
- Available and Unavailable Energy 471 10.2
- 10.3 Availability 477
- 10.4 Surroundings Work 478
- 10.5 Reversible Work and Irreversibility 478
- 10.6 Availability in a Closed System 479
- 10.7 Availability in a SSSF Process in an Open System 483
- Second Law Efficiencies of Processes 489 10.8
  - Second Law Efficiency of Cycles 496 10.9 Problems 501

411

#### 11 THERMODYNAMIC PROPERTY RELATIONS

ŀ	1.	1	Helmhol	tz and	Gibbs	Functions	505

- 11.2 Two Mathematical Conditions for Exact Differentials (Properties) 506
- 11.3 The Maxwell Relations 507
- 11.4 Clapeyron Equation 508
- 11.5 Relations for Changes in Enthalpy, Internal Energy and Entropy 512
- 11.6 Specific Heat Relations 521
- 11.7 Generalized Relations/Charts for Residual Enthalpy and Entropy 524
- 11.8 Gibbs Function at Zero Pressure: A Mathematical Anomaly 533
- 11.9 Fugacity, Fugacity Coefficient and Residual Gibbs Function 534
- 11.10 The Joule-Thomson Coefficient and Inversion Curve 536
- 11.11 Thermodynamic Similarity 542 Problems 545,

#### 116

#### 12 NON-REACTING MIXTURES OF GASES AND LIQUIDS

597

505

12.1 Measures of Composition in Multicomponent Systems 550

#### PART A: GAS MIXTURES

- 12.2 Mixtures of Ideal Gases 551
- 12.3 Gas Vapour Mixtures 558
- 12.4 Application of First Law to Psychrometric Process 568
- 12.5 Real Gas Mixtures 572

#### PART B: LIQUID MIXTURES/SOLUTIONS

- 12.6 Ideal Solutions 575
- 12.7 Real Solutions 576

## PART C: THERMODYNAMIC RELATIONS FOR REAL MIXTURES

- 12.8 Partial Properties 577
- 12.9 Relations for Fugacity and Fugacity Coefficient in Real Gas Mixtures 583
- 12.10 Relations for Activity and Activity Coefficient in Real Liquid Mixtures/Solutions 588 Problems 594

#### 13 PHASE EQUILIBRIUM: VAPOUR LIQUID EQUILIBRIUM OF MIXTURES

- 13.1 Phase Diagrams for Binary Mixtures 597
- 13.2 Vapour–Liquid Equilibrium in Ideal Solutions 602
- 13.3 Criteria of Equilibrium 606

- 13.4 Criterion for Phase Equilibrium 608
- 13.5 Calculation of Standard State Fugacity  $f_i$  of Pure Component *i* 610
- 13.6 Vapour liquid Equilibrium at Low to Moderate Pressures 613
- 13.7 Determination of Constants of Activity Coefficient Equations 613
- 13.8 Enthalpy Calculations 620 Problems 631

#### 14 CHEMICAL REACTIONS AND COMBUSTION

- 14.1 Thermochemistry 637
- 14.2 Measures of Composition in Chemical Reactions 637
- 14.3 Application of First Law of Thermodynamics to Chemical Reactions 638
- 14.4 The Combustion Process: Standard Heat/Enthalpy of Combustion 645
- 14.5 Reactions at Actual Temperatures 652
- 14.6 Adiabatic Flame Temperature 655
- 14.7 Entropy Change of Reacting Systems 656
- 14.8 Application of Second Law of Thermodynamics to Chemical Reactions 662
- 14.9 Fuel Cells 664
- 14.10 Fuels 667
- 14.11 Non-Conventional Fuels 670 Problems 671

#### **15 CHEMICAL EQUILIBRIUM**

- 15.1 Advancement of Chemical Reaction 675
- 15.2 Equilibrium Criterion in Chemical Reactions 677
- 15.3 Equilibrium Constant and Law of Mass Action 679
- 15.4 Equilibrium Constant for Gas Phase Reactions in the Standard State 686
- 15.5 Combustion Generated Pollution 688
- 15.6 Simultaneous Reactions 692 Problems 695

REFERENCES	697
APPENDIX (Tables A.1 to A.18, Mollier Chart for Water)	699
ANSWERS TO SELECTED PROBLEMS	752
INDEX	756

MOLLIER DIAGRAM OF WATER (at the end)

637

# THERMODYNAMICS

Written with an interdisciplinary approach, this book lays emphasis on the fundamental concepts with the aim of developing a profound conceptual base. It brings out interesting data and considerations involved in actual thermodynamic applications.

### **SALIENT FEATURES**

- Carefully devised sequence and integration of topics with step-bystep explanation of fundamentals thereby maintaining clarity of concepts.
- Discusses the practical problems in actual engineering applications.
- A chapter on combined first and second law application to all practical non-flow and flow processes.
- Clearly brings out meaning of the term 'system' whether closed or open type.
- Emphasises distinction between work in a non-flow process in a closed system (pdV) and work in a flow process in an open system (–Vdp).
- Numerous illustrative examples class-tested many times over the last eight years both in India and abroad.

# FROM THE REVIEWER ....

- Comprehensive treatment of topics with a conscious effort to maintain a reasonable level of rigour.
- Follows a sequence different from several standard texts on the subject.
- Extremely well-designed examples and problems.
- Provides useful information regarding the power ratings of common power-producing and power-consuming devices.

Fully meets the requirements of the core course on the subject offered to undergraduate engineering students of all disciplines.

IT LINDARI

1001

#### The McGraw·Hill Companies



Tata McGraw-Hill Publishing Company Limited 7 West Patel Nagar, New Delhi 110 008

Visit our website at : www.tatamcgrawhill.com