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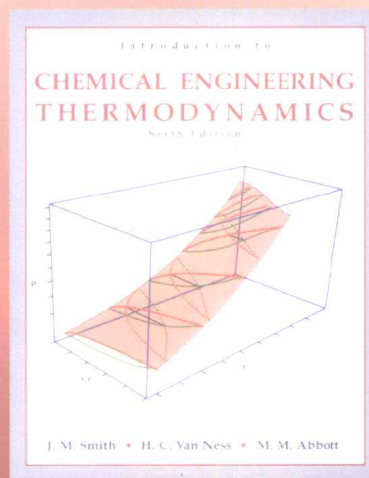
INTRODUCTION TO  
**CHEMICAL  
ENGINEERING  
THERMODYNAMICS**

Sixth Edition

**化工热力学导论**

第六版

J.M.Smith H.C.Van Ness M.M.Abbott



化学工业出版社



Education

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**Chemical Engineering  
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衷心感谢化学工业出版社将本书赠送给我学习。

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## 前 言

随着中国社会主义现代化建设进入新的阶段，以高质量的高等教育培养千百万专门人才，迎接新世纪的挑战，是实现“科教兴国”战略的基础工程，也是完成“十五”计划各项奋斗目标的重要保证。为切实加强高等学校本科教学并提高教学质量，教育部于2001年专门下发文件提出12条意见，对高等学校教学工作从认识、管理、教师队伍到教学方法和教学手段等给予指导。文件强调，按照“教育要面向现代化、面向世界、面向未来”的要求，为适应经济全球化和科技国际化的挑战，本科教育要创造条件使用英语等外语进行公共课和专业课教学。

在文件精神指导下，全国普通高等学校尤其是重点高校中兴起了使用国外教材开展教学活动的潮流。如生物技术与工程、环境科学与工程、材料科学与工程及作为其学科基础理论重要组成部分的化学技术和化学工程技术又是这股潮流中最为活跃的领域之一。在教育部“化工类专业人才培养方案及教学内容体系改革的研究与实践”项目组及“化工类专业创新人才培养模式、教学内容、教学方法和教学改革的研究与实践”项目组和“全国本科化学工程与工艺专业教学指导委员会”的指导和帮助下，化学工业出版社及时启动了引进国外名校名著的教材工程。

出版社组织编辑人员多次赴国外学习考察，通过国外出版研究机构对国外著名的高等学校进行调查研究，搜集了一大批国际知名院校的现用教材选题。他们还联络国内重点高校的专家学者组建了“国外名校名著评价委员会”，对国外和国内高等本科教学进行比较研究，对教材内容质量进行审查评议，然后决定是否引进。他们与国外许多著名的出版机构建立了联系，有的还建立了长期合作关系，以掌握世界范围内优秀教材的出版动态。

以其化学化工专业领域的优势资源为基础，化学工业出版社的教材引进主要涉及化学、化学工程与工艺、环境科学与工程、生物技术与工程、材料科学与工程、制药工程等专业，对过程装备与控制工程、自动化等传统专业教材的引进也在规划之中。

他们在影印、翻译出版国外教材的过程中，注意学习国外教材出版的经验，提高编辑素质，密切编读联系，整合课程体系，更新教材内容，科学设计版面，提高印装质量，更好地为教育服务。

在化工版“国外名校名著”系列教材即将问世之际，我们不仅感谢化学工业出版社为高等教育所做的努力，更应赞赏他们严谨认真的工作作风。

中国科学院院士，天津大学教授

余国琮

2002年8月

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# List of Symbols

$A$	Area
$A$	Molar or specific Helmholtz energy $\equiv U - TS$
$A$	Parameter, empirical equations, e.g., Eq. (4.4), Eq. (6.71), Eq. (12.14)
$a$	Acceleration
$a$	Molar area, adsorbed phase
$\bar{a}$	Parameter, cubic equations of state
$\bar{a}_i$	Partial parameter, cubic equations of state
$B$	Second virial coefficient, density expansion
$B$	Parameter, empirical equations, e.g., Eq. (4.4), Eq. (6.71), Eq. (12.14)
$B'$	Second virial coefficient, pressure expansion
$B^0, B^1$	Functions, generalized second-virial-coefficient correlation
$B_{ij}$	Interaction second virial coefficient
$b$	Parameter, cubic equations of state
$\bar{b}_i$	Partial parameter, cubic equations of state
$C$	Third virial coefficient, density expansion
$C$	Parameter, empirical equations, e.g., Eq. (4.4), Eq. (6.71), Eq. (12.14)
$C'$	Third virial coefficient, pressure expansion
$C_P$	Molar or specific heat capacity, constant pressure
$C_V$	Molar or specific heat capacity, constant volume
$C_P^\circ$	Standard-state heat capacity, constant pressure
$\Delta C_P^\circ$	Standard heat-capacity change of reaction
$\langle C_P \rangle_H$	Mean heat capacity, enthalpy calculations
$\langle C_P \rangle_S$	Mean heat capacity, entropy calculations
$\langle C_P^\circ \rangle_H$	Mean standard heat capacity, enthalpy calculations
$\langle C_P^\circ \rangle_S$	Mean standard heat capacity, entropy calculations
$c$	Speed of sound
$D$	Fourth virial coefficient, density expansion
$D$	Parameter, empirical equations, e.g., Eq. (4.4), Eq. (6.72)
$D'$	Fourth virial coefficient, pressure expansion
$E_i$	Energy level
$E_K$	Kinetic energy
$E_P$	Gravitational potential energy
$F$	Degrees of freedom, phase rule

$F$	Force
$\mathcal{F}$	Faraday's constant
$f_i$	Fugacity, pure species $i$
$f_i^\circ$	Standard-state fugacity
$\hat{f}_i$	Fugacity, species $i$ in solution
$G$	Molar or specific Gibbs energy $\equiv H - TS$
$G_i^\circ$	Standard-state Gibbs energy, species $i$
$\bar{G}_i$	Partial Gibbs energy, species $i$ in solution
$G^E$	Excess Gibbs energy $\equiv G - G^{id}$
$G^R$	Residual Gibbs energy $\equiv G - G^{ig}$
$\Delta G$	Gibbs-energy change of mixing
$\Delta G^\circ$	Standard Gibbs-energy change of reaction
$\Delta G_f^\circ$	Standard Gibbs-energy change of formation
$g$	Local acceleration of gravity
$g_c$	Dimensional constant = $32.1740(\text{lb}_m)(\text{ft})(\text{lb}_f)^{-1}(\text{s})^{-2}$
$g_i$	Degeneracy
$H$	Molar or specific enthalpy $\equiv U + PV$
$\mathcal{H}_i$	Henry's constant, species $i$ in solution
$H_i^\circ$	Standard-state enthalpy, pure species $i$
$\bar{H}_i$	Partial enthalpy, species $i$ in solution
$H^E$	Excess enthalpy $\equiv H - H^{id}$
$H^R$	Residual enthalpy $\equiv H - H^{ig}$
$(H^R)^0, (H^R)^1$	Functions, generalized residual-enthalpy correlation
$\Delta \widetilde{H}$	Enthalpy change ("heat") of mixing; also, latent heat of phase transition
$\widetilde{\Delta H}$	Heat of solution
$\Delta H^\circ$	Standard enthalpy change of reaction
$\Delta H_0^\circ$	Standard heat of reaction at reference temperature $T_0$
$\Delta H_f^\circ$	Standard enthalpy change of formation
$h$	Planck's constant
$l$	Represents an integral, defined, e.g., by Eqs. (6.62)
$I$	First ionization potential
$K_j$	Equilibrium constant, chemical reaction $j$
$K_i$	Vapor/liquid equilibrium ratio, species $i \equiv y_i/x_i$
$k$	Boltzmann's constant
$\mathcal{L}$	Molar fraction of system that is liquid
$l$	Length
$l_{ij}$	Equation-of-state interaction parameter, Eq. (14.97)
$\mathbf{M}$	Mach number
$M$	Molar mass (molecular weight)
$M$	Molar or specific value, extensive thermodynamic property
$\bar{M}_i$	Partial property, species $i$ in solution
$M^E$	Excess property $\equiv M - M^{id}$
$M^R$	Residual property $\equiv M - M^{ig}$
$\Delta M$	Property change of mixing

$\Delta M^\circ$	Standard property change of reaction
$\Delta M_f^\circ$	Standard property change of formation
$m$	Mass
$\dot{m}$	Mass flowrate
$N$	Number of chemical species, phase rule
$N_A$	Avogadro's number
$n$	Number of moles
$\dot{n}$	Molar flowrate
$\tilde{n}$	Moles of solvent per mole of solute
$n_i$	Number of moles, species $i$
$P$	Absolute pressure
$P^\circ$	Standard-state pressure
$P_c$	Critical pressure
$P_r$	Reduced pressure
$P_0$	Reference pressure
$p_i$	Partial pressure, species $i$
$P_i^{\text{sat}}$	Saturation vapor pressure, species $i$
$Q$	Heat
$\dot{Q}$	Rate of heat transfer
$q$	Volumetric flowrate
$q$	Parameter, cubic equations of state
$q$	Electric charge
$\bar{q}_i$	Partial parameter, cubic equations of state
$R$	Universal gas constant (Table A.2)
$r$	Compression ratio
$r$	Intermolecular separation
$r$	Number of independent chemical reactions, phase rule
$S$	Molar or specific entropy
$\bar{S}_i$	Partial entropy, species $i$ in solution
$S^E$	Excess entropy $\equiv S - S^{id}$
$S^R$	Residual entropy $\equiv S - S^{ig}$
$(S^R)^0, (S^R)^1$	Functions, generalized residual-entropy correlation
$\dot{S}_G$	Entropy generation per unit amount of fluid
$\dot{S}_G$	Rate of entropy generation
$\Delta S$	Entropy change of mixing
$\Delta S^\circ$	Standard entropy change of reaction
$\Delta S_f^\circ$	Standard entropy change of formation
$T$	Absolute temperature, kelvins or rankines
$T_c$	Critical temperature
$T_n$	Normal-boiling-point temperature
$T_r$	Reduced temperature
$T_0$	Reference temperature
$T_\sigma$	Absolute temperature of surroundings
$T_i^{\text{sat}}$	Saturation temperature, species $i$
$t$	Temperature, °C or (°F)



$t$	Time
$U$	Molar or specific internal energy
$\mathcal{U}$	Intermolecular pair-potential function
$u$	Velocity
$V$	Molar or specific volume
$\mathcal{V}$	Molar fraction of system that is vapor
$\bar{V}_i$	Partial volume, species $i$ in solution
$V_c$	Critical volume
$V_r$	Reduced volume
$V^E$	Excess volume $\equiv V - V^{id}$
$V^R$	Residual volume $\equiv V - V^{ig}$
$\Delta V$	Volume change of mixing; also, volume change of phase transition
$W$	Work
$\dot{W}$	Work rate (power)
$W_{\text{ideal}}$	Ideal work
$\dot{W}_{\text{ideal}}$	Ideal-work rate
$W_{\text{lost}}$	Lost work
$\dot{W}_{\text{lost}}$	Lost-work rate
$W_s$	Shaft work for flow process
$\dot{W}_s$	Shaft power for flow process
$x_i$	Mole fraction, species $i$ , liquid phase or general
$x^v$	Quality
$y_i$	Mole fraction, species $i$ , vapor phase
$Z$	Compressibility factor $\equiv PV/RT$
$Z_c$	Critical compressibility factor $\equiv P_c V_c / RT_c$
$Z^0, Z^1$	Functions, generalized compressibility-factor correlation
$\mathcal{Z}$	Partition function
$z$	Adsorbed phase compressibility factor, defined by Eq. (14.104)
$z$	Elevation above a datum level
$z_i$	Overall mole fraction or mole fraction in a solid phase

### Superscripts

$E$	Denotes excess thermodynamic property
$av$	Denotes phase transition from adsorbed phase to vapor
$id$	Denotes value for an ideal solution
$ig$	Denotes value for an ideal gas
$l$	Denotes liquid phase
$lv$	Denotes phase transition from liquid to vapor
$R$	Denotes residual thermodynamic property
$s$	Denotes solid phase
$sl$	Denotes phase transition from solid to liquid
$t$	Denotes a total value of an extensive thermodynamic property
$v$	Denotes vapor phase
$\infty$	Denotes a value at infinite dilution

*Greek letters*

$\alpha$	Function, cubic equations of state (Table 3.1, p. 99)
$\alpha$	Polarizability
$\alpha, \beta$	As superscripts, identify phases
$\alpha\beta$	As superscript, denotes phase transition from phase $\alpha$ to phase $\beta$
$\beta$	Volume expansivity
$\beta$	Parameter, cubic equations of state
$\Gamma_i$	Integration constant
$\gamma$	Ratio of heat capacities $C_P/C_V$
$\gamma_i$	Activity coefficient, species $i$ in solution
$\delta$	Polytropic exponent
$\epsilon$	Constant, cubic equations of state
$\epsilon$	Well depth, intermolecular potential function
$\epsilon_0$	Electric permittivity of vacuum
$\epsilon$	Reaction coordinate
$\eta$	Efficiency
$\kappa$	Isothermal compressibility
$\Pi$	Spreading pressure, adsorbed phase
$\Pi$	Osmotic pressure
$\pi$	Number of phases, phase rule
$\mu$	Joule/Thomson coefficient
$\mu$	Dipole moment
$\mu_i$	Chemical potential, species $i$
$\nu_i$	Stoichiometric number, species $i$
$\rho$	Molar or specific density $\equiv 1/V$
$\rho_c$	Critical density
$\rho_r$	Reduced density
$\sigma$	Constant, cubic equations of state
$\sigma$	Molecular collision diameter
$\tau$	Temperature ratio $\equiv T/T_0$ [In Eq. (6.72), $\tau \equiv 1 - T_r$ ]
$\Phi_i$	Ratio of fugacity coefficients, defined by Eq. (14.2)
$\phi_i$	Fugacity coefficient, pure species $i$
$\hat{\phi}_i$	Fugacity coefficient, species $i$ in solution
$\phi^0, \phi^1$	Functions, generalized fugacity-coefficient correlation
$\Psi, \Omega$	Constants, cubic equations of state
$\omega$	Acentric factor

*Notes*

cv	As a subscript, denotes a control volume
fs	As a subscript, denotes flowing streams
o	As a superscript, denotes the standard state
-	Overbar denotes a partial property
.	Overdot denotes a time rate
^	Circumflex denotes a property in solution
$\Delta$	Difference operator

# Preface

The purpose of this text is to present thermodynamics from a chemical-engineering viewpoint. Although the laws of thermodynamics are universal, the subject is most effectively taught in the context of the discipline of student commitment. This is the justification for a separate text for chemical engineers, just as it has been for the previous five editions, which have been in print for more than 50 years.

In writing this text, we have sought to maintain the rigor characteristic of sound thermodynamic analysis, while at the same time providing a treatment that may be understood by the average undergraduate. Much is included of an introductory nature, but development is carried far enough to allow application to significant problems in chemical-engineering practice.

For a student new to this subject a demanding task of discovery lies ahead. New ideas, terms, and symbols appear at a bewildering rate. The challenge, ever present, is to think topics through to the point of understanding, to acquire the capacity to reason, and to apply this fundamental body of knowledge to the solution of practical problems.

The first two chapters of the book present basic definitions and a development of the first law. Chapters 3 and 4 treat the pressure/volume/temperature behavior of fluids and certain heat effects, allowing early application of the first law to realistic problems. The second law and some of its applications are considered in Chap. 5. A treatment of the thermodynamic properties of pure fluids in Chap. 6 allows general application of the first and second laws, and provides for an expanded treatment of flow processes in Chap. 7. Chapters 8 and 9 deal with power production and refrigeration processes. The remainder of the book, concerned with fluid mixtures, treats topics in the unique domain of chemical-engineering thermodynamics. Chapters 11 and 12 provide a comprehensive exposition of the theory and application of solution thermodynamics. Chemical-reaction equilibrium is covered at length in Chap. 13. Chapter 14 deals with topics in phase equilibria, including an extended treatment of vapor/liquid equilibrium, and adsorption and osmotic equilibria. Chapter 15 treats the thermodynamic analysis of real processes, affording a review of much of the practical subject matter of thermodynamics. Finally, Chap. 16 presents an introduction to molecular thermodynamics.

The material of these 16 chapters is more than adequate for an academic-year undergraduate course, and discretion, conditioned by the content of other courses, is required in the choice of what is covered. The first 13 chapters include material thought necessary as part of any chemical engineer's education. Where only a single-semester course in chemical-engineering thermodynamics is provided, these 13 chapters represent sufficient content.

The book is comprehensive enough to make it a useful reference both in graduate courses and for professional practice. However, length considerations make necessary a prudent selectivity. Thus, we have not been able to include certain topics worthy of attention, but of a specialized nature. These include applications to polymers, electrolytes, and biomaterials.

We cannot begin to mention the many persons to whom we are indebted for contributions of various kinds, direct and indirect, over the years during which this text has evolved, edition to edition, into its present form. To all we extend our thanks.

*J. M. Smith*  
*H. C. Van Ness*  
*M. M. Abbott*

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# Chapter 1

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## Introduction

### 1.1 THE SCOPE OF THERMODYNAMICS

The science of thermodynamics was born in the nineteenth century of the need to describe the operation of steam engines and to set forth the limits of what they can accomplish. Thus the name itself denotes power developed from heat, with obvious application to heat engines, of which the steam engine was the initial example. However, the principles observed to be valid for engines are readily generalized, and are known as the first and second laws of thermodynamics. These laws have no proof in the mathematical sense; their validity lies in the absence of contrary experience. Thus thermodynamics shares with mechanics and electromagnetism a basis in primitive laws.

These laws lead through mathematical deduction to a network of equations which find application in all branches of science and engineering. The chemical engineer copes with a particularly wide variety of problems. Among them are calculation of heat and work requirements for physical and chemical processes, and the determination of equilibrium conditions for chemical reactions and for the transfer of chemical species between phases.

Thermodynamic considerations do not establish the *rates* of chemical or physical processes. Rates depend on driving force and resistance. Although driving forces are thermodynamic variables, resistances are not. Neither can thermodynamics, a macroscopic-property formulation, reveal the microscopic (molecular) mechanisms of physical or chemical processes. On the other hand, knowledge of the microscopic behavior of matter can be useful in the calculation of thermodynamic properties.<sup>1</sup> Property values are essential to the practical application of thermodynamics. The chemical engineer deals with many chemical species, and experimental data are often lacking. This has led to development of “generalized correlations” that provide property estimates in the absence of data.

The application of thermodynamics to any real problem starts with the identification of a particular body of matter as the focus of attention. This body of matter is called the *system*, and its thermodynamic state is defined by a few measurable macroscopic properties. These depend on the fundamental *dimensions* of science, of which length, time, mass, temperature, and amount of substance are of interest here.

<sup>1</sup>An elementary treatment is presented in Chap. 16.