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化工热力学导论

(英文改编版)

Introduction to
Chemical Engineering Thermodynamics

(原著第七版)

Seventh Edition

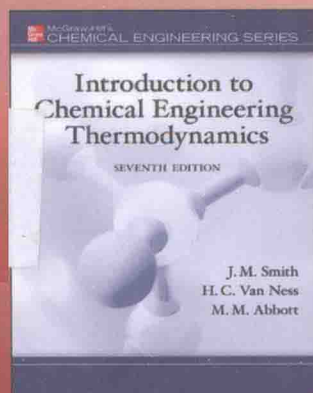
江振西 改编

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· 北京 ·

J. M. Smith, H. C. Van Ness, M. M. Abbott
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改编前言

双语教学是高校学科课程教学改革的一项重要措施,是我国高等教育走向世界的重要途径。为满足开展化工热力学双语教学的需要,笔者在多年化工热力学双语教学探索实践中,改编了 J. M. Smith 等编写的《Introduction to Chemical Engineering Thermodynamics》(Seventh Edition) 作为化工热力学双语教学教材。为尽可能保持与化工热力学中文教学大纲一致,同时适用于双语教学,改编书选取了原版教材的前 13 章内容,对偏理论的少量内容做了删减,并在各章末增加了中文要点提示、化工热力学专业术语词汇双语注释和概念习题。

化学工程发源于西方并以英语构筑和传承了这一学科。本书以原著为基准,在忠实于原著的基础上,对某些概念做了延伸解释,澄清了汉语化工热力学教学中存在的某些模糊概念,改正了一些重要专业词汇的汉语译法,例如 subcooled 的译法从“过冷”改为“亚冷”,并对内容做了梳理、归纳和总结。本书给出了大量的专业词汇英语注释,丰富的专业词汇量为专业交流和沟通架起桥梁。

Smith 等编写的《化工热力学导论》是世界化工领域影响最大、发行范围最广的化工热力学经典教材。原版书叙述严谨、逻辑性强、概念清楚、内容完美、结构合理。这本书从化学工程的角度全面覆盖了热力学这一学科知识,透彻地阐述了热力学原理并详细地叙述了其在化学过程中的应用。并且包含有大量的工业实际问题、例子和插图以帮助读者理解复杂的概念。新想法、新术语和符号不断激励读者思考并鼓励读者使用热力学知识去解决实际问题。

改编后全书主要内容包括以下几个方面:热力学基本概念和基本定律,纯流体的 $P-V-T$ 性质、热效应、纯流体的热力学性质、热力学原理在流动过程中的应用、热功过程、制冷过程、汽液平衡、溶液热力学理论及其应用和化学反应平衡。书中第 1~9 章研究单组分体系,

第 10~13 章研究多组分体系。书中列举了许多理论联系实际的例题，并配有大量来自工业实践的习题。原书第七版以 SI 单位制为主，部分例题和习题采用了英制。考虑到在北美两种单位制仍在并用，为和国际接轨，本书仍保留了使用英制单位的内容。改编后原书的内容从 800 余页缩减为 400 多页，新增内容 200 多页。

新增内容是为帮助读者更好地学习英语原版化工热力学所编写的辅助教学资料。辅助教学资料围绕化工热力学的重点与难点提供了丰富与精辟的解释，期许能够帮助读者理解原版化工热力学的内容，这是本书在双语教学教材建设方面的一项创新性探索工作。改编后的《化工热力学导论》适合用作国内化学工程与工艺专业本科生化工热力学双语课程教材，也可用作化学工程与技术学科研究生以及化学工程领域专业人员的参考书。在双语化工热力学教学实践中，要求学生使用 Mathcad 解题。Mathcad 是一款别具一格的工程计算软件，它集计算、数据可视化与文字处理于一体。使用 Mathcad 求解化工热力学问题编程简单、使用方便，特别是编程与通常书写形式一致，便于思考。通过在双语教学中使用 Mathcad 解题，能使学生拓展视野，学习国外的先进技术，有利于和国际水平保持一致。

本书编写过程中引用了大量网络资源资料，主要有 Wikipedia 和 IndiaBix，参考了《化工热力学导论》第三版和第七版中译本，以及第三版《化工热力学导论》习题解答，在此对网络资源资料的作者和中译本译者表示诚挚感谢。

本书在编撰过程中，得到了郑州大学化工与能源学院化学工程与工艺系同仁们的大力支持，他们是任保增、汤建伟、陈卫航、刘金盾、锥廷亮、刘丽、宋怀俊、万亚珍、张婕、周彩荣、詹自力、靳会杰、廉红蕾、高健和和张亚涛等。天津大学化工学院夏淑倩和大连理工大学化工学院于志家对本书改编部分进行了悉心审读并提出了许多有益和宝贵的修改建议，天津大学马沛生先生对本书的部分内容进行了审读。藉此机会，对他们的建言和帮助表示衷心感谢。

本书出版得到以下项目的资金支持：河南省教育厅 2011 年双语教学示范项目“化工热力学（双语）”，郑州大学 2012 年度校级教学改革研究项目“化工热力学双语课程建设和实践”，郑州大学 2012 年研究生全英语教学课程建设项目“高等化工热力学（全英语）”，郑州大学重点学科建设计划资助项目“化工热力学导论（英文改编版）”。

原书为教师提供了一些网上资源，采用该书作教材的教师可向 McGraw-Hill Education 公司北京代表处联系索取教学课件资料，传真：+86 10 62790292，电子邮件：instructorchina@mcgraw-hill.com。

由于笔者水平有限，书中难免有不当之处，敬请读者批评指正。

江振西 Zhenxi Jiang
2014 年 1 月于郑州大学

Preface

Thermodynamics, one of the central subjects of science, is based on laws of universal applicability. The justification for presenting the subject from a chemical-engineering viewpoint is our conviction that it is most effectively taught in the context of the discipline of student commitment.

Although *introductory* in nature, the material of this text should not be thought simple. Indeed, there is no way to make it simple, and a student new to the subject will find that a demanding task of discovery lies ahead. New concepts, words, and symbols appear at a bewildering rate, and here memory plays a part. A far greater challenge is the necessity to develop a capacity to reason and to apply thermodynamic principles in the solution of practical problems. While maintaining the rigor characteristic of sound thermodynamic analysis, we have made every effort to avoid unnecessary mathematical complexity. Moreover, we encourage understanding by writing simple active-voice, present-tense sentences. We can hardly supply the required motivation, but our objective, as it has been for all previous editions, is a treatment that may be understood by any student willing to exercise due diligence.

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 14^① deals with topics in phase equilibria, including an extended treatment of vapor/liquid equilibrium, and adsorption and

① 英文改编版已删去第 14 章。

osmotic equilibria. Chapter 15^① treats the thermodynamic analysis of real processes, affording a review of much of the practical subject matter of thermodynamics.

The material of these 15^② chapters is more than adequate for an academic-year under-graduate 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 may represent sufficient content.

The laws and principles of classical thermodynamics do not depend on any particular model of the structure of matter; they are free of any molecular considerations. However, the behavior exhibited by matter—gases, liquids, and solids— does depend on its particulate nature, and in Chapter 16^③ we present an introduction to molecular thermodynamics, to which reference is occasionally made in earlier chapters.

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 do not include certain topics worthy of attention, but of a specialized nature. These include applications to polymers, electrolytes, and biomaterials.

We are indebted to many individuals— students, professors, reviewers— who have contributed in various ways to the quality of this seventh edition, directly and indirectly, through question and comment, praise and criticism, over the 55 years and six editions of its evolution. To all we extend our thanks.

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

① 英文改编版已删去第 15 章。

② 英文改编版已删去第 14 和第 15 章。

③ 英文改编版已删去第 16 章。

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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
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^\ominus	Standard-state heat capacity, constant pressure
ΔC_p^\ominus	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
$\langle C_p^\ominus \rangle_H$	Mean standard heat capacity, enthalpy calculations
$\langle C_p^\ominus \rangle_S$	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
F	Faraday's constant
f_i	Fugacity, pure species i
f_i^\ominus	Standard-state fugacity
\hat{f}_i	Fugacity, species i in solution
G	Molar or specific Gibbs energy $\equiv H - TS$
G_i^\ominus	Standard-state Gibbs energy, species i
\bar{G}_i	Partial Gibbs energy, species i in solution
G^E	Excess Gibbs energy $\equiv G - G^{\text{id}}$
G^R	Residual Gibbs energy $\equiv G - G^{\text{ig}}$
ΔG	Gibbs-energy change of mixing
ΔG^\ominus	Standard Gibbs-energy change of reaction
ΔG_f^\ominus	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^\ominus	Standard-state enthalpy, pure species i
\bar{H}_i	Partial enthalpy, species i ; in solution
H^E	Excess enthalpy $\equiv H - H^{\text{id}}$
H^R	Residual enthalpy $\equiv H - H^{\text{ig}}$
$(H^R)^0, (H^R)^1$	Functions, generalized residual-enthalpy correlation
ΔH	Enthalpy change ("heat") of mixing; also, latent heat of phase transition
$\widetilde{\Delta H}$	Heat of solution
ΔH^\ominus	Standard enthalpy change of reaction
ΔH_0^\ominus	Standard heat of reaction at reference temperature T_0
ΔH_f^\ominus	Standard enthalpy change of formation
h	Planck's constant
I	Represents an integral, defined, e.g., by Eq. (6.62)
I	First ionization potential
K_j	Equilibrium constant, chemical reaction j
K_i	Vapor-liquid equilibrium ratio, species $i \equiv y/x_i$
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)
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 $\equiv M - M^{\text{id}}$
M^R	Residual property $\equiv M - M^{\text{ig}}$
ΔM	Property change of mixing
ΔM^\ominus	Standard property change of reaction
ΔM_f^\ominus	Standard property change of formation
n	Mass
\dot{n}	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^\ominus	Standard-state pressure
P_c	Critical pressure
P_r	Reduced pressure
P_0	Reference pressure
p_i	Partial pressure, species i
P_i^{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 $\equiv S - S^{\text{id}}$

S^R	Residual entropy $\equiv S - S^{\text{ig}}$
$(S^R)^0, (S^R)^1$	Functions, generalized residual-entropy correlation
S_G	Entropy generation per unit amount of fluid
\dot{S}_G	Rate of entropy generation
ΔS	Entropy change of mixing
ΔS^\ominus	Standard entropy change of reaction
ΔS_f^\ominus	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_σ	Absolute temperature of surroundings
T_i^{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 $\equiv V - V^{\text{id}}$
V^R	Residual volume $\equiv V - V^{\text{ig}}$
ΔV	Volume change of mixing; also, volume change of phase transition
W	Work
\dot{W}	Work rate(power)
W_{ideal}	Ideal work
\dot{W}_{ideal}	Ideal-work rate
W_{lost}	Lost work
\dot{W}_{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
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

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
∞	Denotes a value at infinite dilution

Greek letters

α	Function, cubic equations of state (Table 3.1)
α	Polarizability
α, β	As superscripts, identify phases
$\alpha\beta$	As superscript, denotes phase transition from phase α to phase β
β	Volume expansivity
β	Parameter, cubic equations of state
Γ_i	Integration constant
γ	Ratio of heat capacities C_p/C_v
γ_i	Activity coefficient, species i in solution
δ	Polytropic exponent
ε	Constant, cubic equations of state
ε	Well depth, intermolecular potential function
ε_0	Electric permittivity of vacuum
ε	Reaction coordinate
η	Efficiency
κ	Isothermal compressibility
Π	Spreading pressure, adsorbed phase