

INTERNATIONAL STUDIES
in SCIENCE and ENGINEERING

Roman Weber

COMBUSTION FUNDAMENTALS

with

Elements of Chemical Thermodynamics



Prof. Dr.-Ing. Roman Weber
Technische Universität Clausthal
Institut für Energieverfahrenstechnik und Brennstofftechnik (IEVB)
Agricolastrasse 4, 38 678 Clausthal-Zellerfeld, Germany
roman.weber@ievb.tu-clausthal.de

Weber, Roman:

Combustion Fundamentals with Elements of Chemical Thermodynamics
Clausthal-Zellerfeld: Papierflieger 2008
ISBN 978-3-89720-921-3

Bibliografische Information der Deutschen Bibliothek

Die Deutsche Bibliothek verzeichnet diese Publikation in der Deutschen Nationalbibliografie; detaillierte bibliografische Daten sind im Internet über <http://dnb.ddb.de> abrufbar.

INTERNATIONAL STUDIES in SCIENCE and ENGINEERING

Editor in Chief:

Prof. Dr.-Ing. Roman Weber, Clausthal University of Technology (Germany)

Editorial Board:

Dr.-Ing. Rüdiger Alt, Clausthal University of Technology (Germany)

Prof. Dr.-Ing. Ryszard Bialecki, Silesian University of Technology (Poland)

Prof. Xu Delong, Xi'an University of Architecture and Technology (China)

Prof. Dr. Peter v. Dierkes, former President of Berliner Stadtreinigungsbetriebe (Germany)

Dipl.-Math. Marc Muster, Clausthal University of Technology (Germany)

Prof. Dr.-Ing. Andrzej Nowak, Silesian University of Technology (Poland)

Prof. Dr.-Ing. Reinhard Scholz, Clausthal University of Technology (Germany)

First Edition 2008

Copyright by PAPIERFLIEGER, Clausthal-Zellerfeld 2008, Telemannstr. 1, 38678 Clausthal-Zellerfeld, Tel.: 05323/96746, <http://www.papierflieger-verlag.de>

No part of this publication may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying, recording, or any information storage and retrieval system, without the prior permission in writing from the publisher.

ISBN 978-3-89720-921-3

The cover of this textbook has been designed using photographs provided by Mr. Marc Muster of TU Clausthal.

Contents

1	Stoichiometry	1
1.1	Introduction	1
1.2	Definitions	4
1.2.1	Chemical Reactions, Atoms and Molecules in Combustion	4
1.2.2	Amount of Substances, Mole and Mass Fractions	5
1.2.3	Density and Concentration (Molar density)	6
1.2.4	Equation of State for Gases and Gas Mixtures	7
1.3	Combustion Stoichiometry for Gaseous Fuels	8
1.3.1	Stoichiometric combustion	8
1.3.2	Excess air ratio (air equivalence ratio) and fuel equivalence ratio	9
1.3.3	Minimum air requirement for a mixture of gaseous fuels	11
1.3.4	Composition of combustion products	11
1.4	Combustion stoichiometry for liquid and solid fuels	16
1.4.1	Minimum oxygen and air requirements and excess air ratio	17
1.4.2	Combustion products	17
1.5	Humid Combustion Air	24
1.5.1	Absolute and relative humidity	24
1.5.2	Dew Point Temperature of Combustion Products	29
1.6	Combustibles burnout for solid fuels	31
1.7	Sub-stoichiometric combustion to carbon dioxide and water vapour	32
1.8	Summary	34
2	Mass and Energy Balance	35
2.1	General Formulation of Mass and Energy Balance	35
2.1.1	Mass and Energy Balance at an Instant	36
2.1.2	Mass and Energy Balance over a Time Interval	37
2.1.3	Mass and Energy Balance under Steady-State Conditions	38
2.1.4	Example of a Mass Balance of a Furnace	38
2.2	The First Law of Thermodynamics	43
2.2.1	System Energy	46
2.2.2	Energy Entering and Leaving the System	49

2.2.3	Energy Balance of Thermal Systems (Machines)	56
2.3	Energy Released in Chemical Reactions	60
2.3.1	Reaction Enthalpy	60
2.3.2	Standard Enthalpies of Formation	62
2.3.3	Lower Calorific Value (LCV) and Gross Calorific Value (GCV)	65
2.3.4	Relationships between Calorific Values, Reaction Enthalpies and Formation Enthalpies	67
2.3.5	Dependence of LCV on Temperature	69
2.3.6	Example of an Energy Balance of a Furnace	72
2.4	Temperature of Adiabatic Combustion	79
2.5	Furnace Exit Temperature	81
2.6	Summary	86
3	Equilibrium Thermodynamics	89
3.1	Irreversible and Reversible Processes	90
3.2	Entropy	96
3.2.1	Entropy of Liquids and Solids	102
3.2.2	Entropy of Ideal Gases	102
3.2.3	Entropy of Phase Transition at the Transition Temperature	103
3.2.4	The Third Law of Thermodynamics	104
3.2.5	Absolute Entropy of Pure Substances	104
3.3	The Second Law of Thermodynamics	107
3.3.1	The Increase in Entropy Principle	107
3.3.2	Entropy Change for a Continuous Process at Steady-State .	110
3.3.3	Irreversibility of Processes	111
3.4	General Conditions for Thermodynamic Equilibrium	112
3.4.1	Isolated System	112
3.4.2	Non-Adiabatic System	113
3.5	Equilibrium Between Phases	116
3.5.1	Single-Component System Consisting of Two Phases	116
3.5.2	Phase Transformations of a Pure Substance	119
3.5.3	Dependence of Gibbs Free Enthalpy on Temperature and Pressure	122
3.5.4	Equilibrium in Multi-Component Single-Phase Systems . .	126
3.5.5	Chemical Potential of Pure Substances	130
3.5.6	Significance of Chemical Potential	131
3.6	Multi-Component, Multi-Phase Systems	134
3.6.1	The Phase Rule	138
3.7	Thermodynamics of Mixing	138

3.8	Summary	146
4	Chemical Equilibrium	149
4.1	Definition of Chemical Equilibrium	150
4.2	Single Chemical Reaction	150
4.2.1	Extent of a Single Reaction	150
4.2.2	Change of Gibbs Enthalpy as a Chemical Reaction Advances	153
4.2.3	Gibbs Enthalpy of Selected Reactions	156
4.2.4	Thermodynamic Equilibrium Constant for a Gaseous Reaction	159
4.2.5	Other Equilibrium Constants	165
4.2.6	Effect of Pressure and Temperature on Thermodynamic Equilibrium Constant	167
4.2.7	Chemical Equilibrium in Presence of a Solid Phase	171
4.2.8	Le Châtelier's Principle	176
4.3	Multiplicity of Chemical Reactions	183
4.3.1	Multi-Component, Multi-Phase Systems with Chemical Reactions	184
4.3.2	Choice of Chemical Reactions	188
4.3.3	Exact Number of Chemical Reactions Needed for Equilibrium Determination	189
4.3.4	Linear Dependence of a Reaction Set	193
4.3.5	The Phase Rule for a System with Chemical Reactions	196
4.4	Equilibrium Composition	200
4.4.1	Systems with a one-dimensional reaction basis	200
4.4.2	Systems with a two-dimensional reaction basis	209
4.4.3	Systems with a multi-dimensional reaction basis	216
4.5	Summary	219
5	Elements of Chemical Kinetics	221
5.1	Introduction	221
5.2	Rate Laws and Reaction Orders	222
5.3	Forward and Reverse Reactions	226
5.4	Elementary Reactions and Reaction Molecularity	231
5.5	Rate of Reactions	237
5.5.1	Temperature dependence of rate coefficients	238
5.5.2	Pressure dependence of rate coefficients	240
5.6	Summary	241
6	Mechanisms of Basic Combustion Reactions	243

Contents

6.1	Chain Reactions	243
6.2	Combustion of Carbon Monoxide (CO)	245
6.3	Combustion of Hydrogen (H ₂)	246
6.3.1	Simplified ignition mechanism	248
6.4	Combustion of Methane (CH ₄)	251
6.5	Methods of Solving Chemical Kinetic Rate Equations	253
6.5.1	Analytical solutions	254
6.5.2	Numerical Solutions	264
6.6	Summary	279
	Gaussian Elimination	283
	Vocabulary	287