

# Heat Pumps in Chemical Process Industry

**Anton A. Kiss**  
**Carlos A. Infante Ferreira**

 **CRC Press**  
Taylor & Francis Group  
Boca Raton London New York

---

CRC Press is an imprint of the  
Taylor & Francis Group, an **Informa** business

---

# Contents

---

Preface, xv

Authors, xix

CHAPTER 1 ■ Introduction to Heat Pumps	1
1.1 INTRODUCTION	1
1.2 HISTORICAL PERSPECTIVE	2
1.3 WORKING PRINCIPLE	4
1.4 EFFICIENCY AND PERFORMANCE	6
1.5 HEAT SOURCES AND SINKS	7
1.6 HEATING, VENTILATING AND AIR CONDITIONING APPLICATIONS	9
1.7 HEAT PUMP TYPES AND INDUSTRIAL APPLICATIONS	10
1.7.1 Compression Heat Pumps	11
1.7.2 Transcritical Heat Pumps	13
1.7.3 Absorption Heat Pumps	14
1.7.4 Heat Transformers	14
1.7.5 Hybrid Heat Pumps	15
1.7.6 Adsorption Heat Pumps	16
1.7.7 Solid-State Heat Pumps	16
1.8 FEASIBILITY CHECK	18
1.9 CONCLUDING REMARKS	19
LIST OF SYMBOLS	19
REFERENCES	20
CHAPTER 2 ■ Thermodynamics of Heat Pump Cycles	23
2.1 INTRODUCTION	23
2.2 FUNDAMENTALS OF THERMODYNAMICS	24

2.2.1	Laws of Thermodynamics	24
2.2.2	Free Energy Functions	30
	2.2.2.1 <i>Pressure and Temperature Dependency of Gibbs Free Energy</i>	32
2.2.3	Phase Equilibrium Condition	33
	2.2.3.1 <i>Pure Components</i>	33
	2.2.3.2 <i>Mixtures</i>	34
2.2.4	Gibbs–Duhem Equation	35
2.2.5	Network of Thermodynamic Properties	36
2.2.6	Fugacity	38
	2.2.6.1 <i>Fugacity Calculation for Pure Components</i>	40
	2.2.6.2 <i>Fugacity Calculations for Mixtures</i>	42
2.3	EQUATIONS OF STATE	42
2.3.1	Virial Family of Equations of State	42
	2.3.1.1 <i>Virial EOS</i>	42
	2.3.1.2 <i>Benedict, Webb, and Rubin EOS</i>	43
	2.3.1.3 <i>Benedict–Webb–Rubin–Lee–Starling EOS</i>	43
	2.3.1.4 <i>Lee–Kesler Method</i>	43
2.3.2	Cubic Equations of State	44
	2.3.2.1 <i>van der Waals EOS</i>	44
	2.3.2.2 <i>Redlich and Kwong EOS</i>	44
	2.3.2.3 <i>Soave–Redlich–Kwong EOS</i>	45
	2.3.2.4 <i>Peng and Robinson EOS</i>	45
	2.3.2.5 <i>Cubic Plus Association EOS</i>	45
	2.3.2.6 <i>Nonpolar Mixtures</i>	46
	2.3.2.7 <i>Polar Fluids</i>	48
	2.3.2.8 <i>Peng–Robinson–Stryjek–Vera EOS</i>	49
2.3.3	EOS Based on Molecular Modeling	50
	2.3.3.1 <i>Statistical Associating Fluid Theory EOS</i>	50
	2.3.3.2 <i>Perturbed-Chain Statistical Associating Fluid Theory EOS</i>	50
2.4	PVT BEHAVIOR AND RELATIONSHIPS	51
2.4.1	Phase Diagrams	51
2.4.2	Property Charts	53
2.4.3	Thermodynamic Cycles	53
2.4.4	Departure Functions	56
	2.4.4.1 <i>Evaluation of Departure Functions</i>	58

2.4.4.2	<i>Equations of State</i>	59
2.4.4.3	<i>Corresponding States</i>	60
2.5	VAPOR/GAS-LIQUID EQUILIBRIUM	61
2.5.1	Ideal Solution Concept	61
2.5.2	Equation-of-State Approach	63
2.5.3	Liquid Activity Coefficient Approach	65
2.5.4	Gas-Liquid Equilibrium	69
2.5.4.1	<i>Asymmetric Definition of Equilibrium Constants</i>	69
2.5.4.2	<i>Cubic EOS Approach</i>	71
2.6	LIQUID ACTIVITY MODELS	71
2.6.1	Modeling Excess Gibbs Free Energy	71
2.6.2	Correlation Models for Liquid Activity	71
2.6.2.1	<i>Margules</i>	72
2.6.2.2	<i>van Laar</i>	72
2.6.2.3	<i>Wilson</i>	73
2.6.2.4	<i>Non-Random Two Liquids</i>	74
2.6.2.5	<i>Universal Quasi-Chemical</i>	75
2.6.3	Predictive Methods for Liquid Activity	75
2.6.3.1	<i>Regular Solution Theory</i>	76
2.6.3.2	<i>UNIQUAC Functional Group Activity Coefficients</i>	76
2.6.3.3	<i>Joback-Reid</i>	78
2.6.3.4	<i>Models Based on Quantum Mechanics</i>	78
2.7	COMBINED EOS AND LACT MODELS	79
2.7.1	$G^{ex}$ Mixing Rules	79
2.7.2	Predictive EOS- $G^{ex}$ Models	80
2.8	PROPERTY MODEL SELECTION AND PARAMETER REGRESSION	81
2.8.1	Selection of Property Models	81
2.8.2	Regression of Parameters	83
2.8.3	Thermodynamic Consistency	84
2.8.4	Statistical Methods	85
2.8.4.1	<i>Least Square Regression</i>	85
2.8.4.2	<i>Maximum Likelihood Approach</i>	86
2.8.5	Evaluation of Models	87
2.9	CONCLUDING REMARKS	88
	LIST OF SYMBOLS	89
	REFERENCES	92

CHAPTER 3 ■ Entropy Production and Exergy Analysis	97
3.1 INTRODUCTION	97
3.2 FIRST AND SECOND LAW EFFICIENCY AND SUSTAINABILITY CRITERIA	97
3.3 SECOND LAW ANALYSIS	102
3.4 EXERGY ANALYSIS OF HEAT PUMP CYCLES	104
3.4.1 Heat Pump Cycle Components	105
3.4.2 Exergy Efficiency of the Cycle	106
3.4.3 Application Example	107
3.4.4 Impact of Malfunction	111
3.5 EXERGY ANALYSIS OF HEAT PUMP PLANT	113
3.6 ENTROPY PRODUCTION ANALYSIS OF HEAT PUMP CYCLE	114
3.6.1 Entropy Production and Heat Pump COP	114
3.6.2 Entropy Production in the Components of the Heat Pump	116
3.7 REDUCING EXERGY LOSSES/ENTROPY PRODUCTION	118
3.7.1 Cycle Level	118
3.7.2 Condenser	119
3.7.3 Evaporator	120
3.7.4 Compressor	121
3.7.5 Expansion Device	121
3.8 CONCLUDING REMARKS	122
LIST OF SYMBOLS	122
REFERENCES	124
CHAPTER 4 ■ Pinch Analysis and Process Integration	125
4.1 INTRODUCTION	125
4.2 PINCH ANALYSIS	126
4.2.1 Basic Concepts	127
4.2.2 Pinch Technology Approach	131
4.3 MINIMUM ENERGY AND CAPITAL COST TARGETS	133
4.3.1 Composite Curves	134
4.3.1.1 Stream Data	134
4.3.2 Pinch Point Principle	141
4.3.3 Balanced Composite Curves	142
4.3.4 Stream Segmentation	142
4.3.5 Thermal Data Extraction	143

4.3.6	Targets for Energy and Capital Cost	144
4.3.6.1	<i>Number of Heat Exchange Units</i>	144
4.3.6.2	<i>Heat Exchange Area</i>	144
4.3.6.3	<i>Number of Shells</i>	145
4.4	PLACEMENT OF UTILITIES	146
4.4.1	Threshold Problems	146
4.4.2	Multiple Utilities	147
4.4.3	Variable Temperature Utilities	148
4.5	HEAT EXCHANGER NETWORK DESIGN	149
4.5.1	Topological Analysis	150
4.5.1.1	<i>Number of Matches</i>	150
4.5.1.2	<i>Paths and Loops</i>	150
4.5.2	HEN Design in the Grid Diagram	151
4.5.3	Stream Splitting	152
4.5.4	Reducing the Heat Exchanger Network	153
4.5.5	Network Optimization	154
4.6	TOTAL SITE INTEGRATION	156
4.6.1	Process Utilities	156
4.6.2	Site Integration	157
4.7	MATHEMATICAL PROGRAMMING	158
4.8	CONCLUDING REMARKS	159
	LIST OF SYMBOLS	160
	REFERENCES	162
CHAPTER 5 ■ Selection of Heat Pumps		163
5.1	INTRODUCTION	163
5.2	THERMAL AND HYDRAULIC REQUIREMENTS	163
5.3	TEMPERATURE LIFT AND SYSTEM IRREVERSIBILITIES	165
5.3.1	Temperature Lift and System Performance	165
5.3.2	Temperature-Driving Forces in the Heat Exchangers of Heat Pumps	169
5.3.3	Nonisentropic Compression Processes	172
5.3.4	Absorption Heat Pumps	174
5.3.5	Other Loss Mechanisms	176
5.3.6	Example of the Impact of Irreversibilities	176
5.3.7	Savings from Energetic Performance	178

5.4	SELECTION OF HEAT PUMPS	178
5.5	HEAT PUMP TYPES	179
5.6	INVESTMENT COSTS	182
5.6.1	Size of Heat Exchangers	182
5.7	COMPARISON OF THE PERFORMANCE OF DIFFERENT CYCLES	184
5.8	OTHER RELEVANT CRITERIA	184
5.9	CONCLUDING REMARKS	185
	LIST OF SYMBOLS	186
	REFERENCES	187
<b>CHAPTER 6 ■ Mechanically Driven Heat Pumps</b>		<b>189</b>
6.1	INTRODUCTION	189
6.2	VAPOR COMPRESSION HEAT PUMPS	190
6.2.1	Reversible Cycle and Efficiency	190
6.2.2	Theoretical Cycle	193
6.2.3	Isobars in a $T$ - $s$ Diagram	195
6.2.4	Processes in Practical Cycle	196
6.2.4.1	<i>Compression</i>	196
6.2.4.2	<i>Condensation</i>	197
6.2.4.3	<i>Expansion Process</i>	197
6.2.4.4	<i>Evaporation</i>	198
6.2.5	Causes of Losses and Possible Improvements	199
6.2.5.1	<i>Pressure-Enthalpy Diagram</i>	200
6.2.5.2	<i>Impact of Compressor</i>	200
6.2.5.3	<i>Impact of the Throttling Process</i>	202
6.2.5.4	<i>Effect of the Evaporating Temperature</i>	204
6.2.5.5	<i>Effect of Condensation Temperature</i>	205
6.2.5.6	<i>Effect of Subcooling</i>	206
6.2.5.7	<i>Effect of Superheating</i>	206
6.2.5.8	<i>Combined Subcooling and Superheating</i>	207
6.2.6	Sizing the System	208
6.2.7	Multistage Operation	215
6.3	VAPOR RECOMPRESSION HEAT PUMPS	220
6.3.1	Theoretical Cycle	220
6.3.2	System Components	222

6.3.3	Operating Conditions and Temperature Lift	223
6.3.4	Stage of Development	224
6.3.5	Performance	224
6.3.6	Part-Load Operation	224
6.4	COMPRESSION RESORPTION HEAT PUMPS	224
6.4.1	Technology Description	224
6.4.2	System Components	227
6.4.3	Operating Conditions and Temperature Lift	228
6.4.4	Stage of Development	231
6.5	TRANSCRITICAL VAPOR COMPRESSION HEAT PUMPS	232
6.5.1	Technology Description	232
6.5.2	Optimal Heat Rejection Pressure in Transcritical Cycles	233
6.5.3	Ways to Improve the Performance of Transcritical Cycles	234
6.5.4	Stage of Development	236
6.6	STIRLING HEAT PUMPS	236
6.6.1	Technology Description	236
6.6.2	Basic Thermodynamics	239
	6.6.2.1 <i>Second-Order Analysis</i>	243
	6.6.2.2 <i>Third-Order Analysis</i>	244
6.6.3	Thermodynamic Losses	245
6.6.4	Heat Pump Cycle Performance	246
6.6.5	Working Fluid Selection	246
6.6.6	Stage of Development	248
6.7	CONCLUDING REMARKS	249
	LIST OF SYMBOLS	250
	REFERENCES	251
CHAPTER 7 ■ Thermally Driven Heat Pumps		255
7.1	INTRODUCTION	255
7.2	LIQUID-VAPOR ABSORPTION HEAT PUMPS	256
7.2.1	Reversible Cycle and Efficiency	256
7.2.2	Theoretical Cycle	265
	7.2.2.1 <i>Nonideal Internal Heat Exchange</i>	266
	7.2.2.2 <i>Incomplete Absorption</i>	267
	7.2.2.3 <i>Incomplete Rectification</i>	268



7.2.2.4	<i>Incomplete Evaporation</i>	269
7.2.2.5	<i>Incomplete External Heat Exchange</i>	269
7.2.2.6	<i>Pressure Drop</i>	270
7.2.2.7	<i>Presence of Noncondensable Gases</i>	271
7.2.3	Sizing the System	272
7.2.3.1	<i>Example with Ammonia-Water</i>	273
7.2.3.2	<i>Example with Water-Lithium Bromide</i>	282
7.2.4	Multieffect Operation	285
7.2.4.1	<i>Double-Effect Example with Water-Lithium Bromide</i>	286
7.2.5	Multistage Operation	290
7.2.6	Stage of Development	291
7.3	SOLID-VAPOR ADSORPTION HEAT PUMPS	291
7.3.1	Physical Adsorption	293
7.3.2	Chemical Adsorption	298
7.3.3	Multieffect Operation	300
7.3.4	Stage of Development	300
7.4	EJECTOR-BASED HEAT PUMPS	302
7.4.1	Technology Description	302
7.4.2	Heat Pump Efficiency	304
7.4.3	Sizing the Ejector	304
7.4.3.1	<i>Model of Motive Nozzle Flow</i>	305
7.4.3.2	<i>Model of Suction Nozzle Flow</i>	307
7.4.3.3	<i>Model of Mixing Section Flow</i>	308
7.4.3.4	<i>Model of the Diffusor Flow</i>	311
7.4.3.5	<i>External Input Parameters</i>	312
7.4.4	Stage of Development	312
7.5	CONCLUDING REMARKS	314
	LIST OF SYMBOLS	314
	REFERENCES	316
CHAPTER 8 ■ Solid-State Heat Pumps		319
8.1	INTRODUCTION	319
8.2	MAGNETIC HEAT PUMPS	320
8.2.1	Magnetocaloric Effect	320
8.2.2	Thermodynamics of MCE	322

8.2.3	Thermodynamic Cycle	325
8.2.3.1	<i>Carnot Cycle</i>	325
8.2.3.2	<i>Brayton Cycle</i>	326
8.2.3.3	<i>Ericsson Cycle</i>	327
8.2.3.4	<i>Cascade Magnetic Cycles</i>	327
8.2.3.5	<i>Active Magnetic Regenerator Cycle</i>	327
8.2.4	Working Materials	328
8.2.5	Stage of Development	330
8.3	THERMOELECTRIC HEAT PUMPS	331
8.3.1	Thermoelectric Effect	332
8.3.1.1	<i>Seebeck Effect</i>	333
8.3.1.2	<i>Peltier Effect</i>	333
8.3.1.3	<i>Thomson Effect</i>	334
8.3.1.4	<i>Joule Heating</i>	335
8.3.1.5	<i>Fourier Heat Conduction</i>	336
8.3.2	Figure of Merit and Performance	337
8.3.3	Stage of Development	338
8.4	THERMOACOUSTIC HEAT PUMPS	340
8.4.1	Thermoacoustic Effect	340
8.4.2	Thermodynamic Cycle	342
8.4.3	Thermoacoustic Technology	343
8.4.4	Stage of Development	344
8.5	CONCLUDING REMARKS	346
	LIST OF SYMBOLS	347
	REFERENCES	349
<b>CHAPTER 9 ■ Industrial Applications of Heat Pumps</b>		<b>351</b>
9.1	INTRODUCTION	351
9.2	APPLICATION OF INDUSTRIAL HEAT PUMPS	351
9.3	WASTE HEAT RECOVERY USING HEAT PUMPS	356
9.4	HEAT PUMP-ASSISTED DISTILLATION	357
9.4.1	Feasibility of Heat Pump-Assisted Distillation	359
9.4.2	Heat Pump-Assisted Distillation Configurations	360
9.4.3	Applications of Heat Pump-Assisted Distillation	361
9.4.4	Selection Scheme for Heat Pump-Assisted Distillation	365

9.4.4.1	<i>Methanol-Water Separation</i>	369
9.4.4.2	<i>Propane-Propylene Splitting</i>	370
9.5	CONCLUDING REMARKS	370
	LIST OF SYMBOLS	371
	REFERENCES	372
<b>CHAPTER 10 ■ Case Studies</b>		<b>375</b>
10.1	INTRODUCTION	375
10.2	VAPOR RECOMPRESSION HEAT PUMP	375
10.2.1	Conventional Extractive Distillation Process	376
10.2.2	Vapor Recompression-Assisted Extractive DWC	377
10.2.3	Sensitivity Analysis of VRC System	380
10.2.4	Economic Evaluation and Process Comparison	381
10.3	VAPOR COMPRESSION HEAT PUMP FOR HEAT RECOVERY	383
10.4	COMPRESSION-RESORPTION HEAT PUMP	389
10.5	ABSORPTION HEAT PUMP	392
10.6	EJECTOR HEAT PUMP	396
10.7	CONCLUDING REMARKS	399
	LIST OF SYMBOLS	400
	REFERENCES	402
INDEX, 405		