
Contents

Preface	xi
Chapter 1. Correlations for the Estimation of Thermodynamic Properties of Pure Substances in the Liquid, Perfect Gas or Vapor–Liquid States	1
1.1. Introduction.	1
1.2. Thermodynamics of the vapor–liquid equilibrium of a pure substance: what should be remembered.	2
1.2.1. Phase-intensive variables and global-intensive variables	2
1.2.2. Conditions of two-phase equilibrium of a pure substance	5
1.2.3. Why should the intensive properties of the liquid and vapor phases of a pure substance in vapor–liquid equilibrium be seen as temperature functions?	5
1.2.4. Critical point of a pure substance	9
1.2.5. Isotherms of a pure species in the fluid region.	9
1.2.6. Property changes on vaporization	11
1.3. Correlations for the saturated vapor pressure of pure substances	12
1.3.1. Practical expressions for the saturated vapor pressure deduced from the Clapeyron equation	12
1.3.2. Empirical expressions (Antoine, Wagner, Frost–Kalkwarf).	17
1.3.3. Taking things further: constraints on the curvature of the graphical representation of $\ln P^{\text{sat}}$ versus $1/T$	17
1.3.4. Focus on the Antoine equation	20
1.4. Equations that can be used to correlate the molar volumes of pure liquids	22
1.4.1. Correlations that can be used for molar volumes of saturated liquids	22

1.4.2. Correlations that can be used for molar volumes of subcooled liquids	24
1.5. Equations that can be used to correlate the molar volumes of saturated gases	25
1.6. Equations that can be used to correlate the enthalpies of vaporization	26
1.6.1. Use of the Clapeyron equation	26
1.6.2. Expression involving many adjustable parameters	27
1.7. Equations used to correlate the heat capacity at constant molar pressure, molar enthalpy or molar entropy of an incompressible liquid	27
1.8. Equations that can be used to correlate the molar heat capacity at constant pressure, molar enthalpy or molar entropy of a perfect gas	29
1.9. Density of a pure substance	32
1.10. Prediction of the thermodynamic properties of pure substances	32
Chapter 2. Estimation of Thermodynamic Properties of Pure Substances Using an Equation of State: Overview of Available Models and Calculation Procedures	35
2.1. Volumetric equation of state: a definition	35
2.2. General overview of the volumetric equations of state	35
2.3. Presentation of usual volumetric equations of state	36
2.3.1. Virial expansion.	36
2.3.2. Classic cubic equations of state.	40
2.3.3. Introduction of volume translation in cubic equations of state with the aim of improving estimation of liquid densities	47
2.3.4. Equations of state relying on the statistical associating fluid theory (SAFT)	51
2.3.5. Equations of state specific to particular pure substances	54
2.4. Practical use of volumetric equations of state.	56
2.4.1. Calculation of the state properties	56
2.4.2. Vapor–liquid equilibrium	56
2.5. Calculation of state properties using a volumetric equation of state	56
2.5.1. Calculation of residual-TP properties	59
2.5.2. Calculation of residual-TV properties	61
2.5.3. Calculation of state-property changes	64
2.6. Vapor–liquid equilibrium calculation using a pressure-explicit equation of state: illustration with cubic equations of state	66

2.6.1. Shapes of isotherms produced by cubic equations of state in the pressure–molar volume plane: link between the form of isotherms and the resolution of cubic equations of state	66
2.6.2. Stable, metastable, unstable roots	68
2.6.3. Graphical determination of the saturated vapor pressure by the Maxwell equal area rule.	71
2.6.4. Plot of the stable portions of an isotherm from an equation of state	73
2.6.5. Calculation of the vaporization properties using an equation of state	74
2.7. Overall summary: criteria for selecting an equation of state for modeling of the thermodynamic properties of a given pure fluid	75

Chapter 3. Low-Pressure Vapor–Liquid and Liquid–Liquid Equilibria of Binary Systems: Activity-Coefficient Models

3.1. Introduction.	77
3.2. Classification of fluid-phase behaviors of binary systems at low pressure and low temperature	78
3.2.1. Conventions for representation of isobaric and isothermal phase diagrams of binary systems	79
3.2.2. The four types of vapor–liquid equilibrium (VLE) diagrams for low temperature, low pressure	81
3.2.3. Five types of liquid–liquid equilibrium (LLE) diagrams.	86
3.2.4. Fluid-phase diagrams resulting from the overlap of LLE and VLE domains. Liquid–liquid–vapor equilibria (VLLE)	92
3.3. Condition of equilibrium between fluid phases of binary systems	100
3.4. Vapor–liquid equilibrium relationship at low pressure	101
3.4.1. Estimation of the fugacity coefficient of a pure substance, present in the expression of function C_i	103
3.4.2. Estimation of the fugacity coefficient of a component in a mixture, present in the expression of function C_i	104
3.4.3. Estimation of the Poynting factor, present in the expression of the function C_i	105
3.4.4. Estimation of the C_i term	105
3.5. Activity coefficients: definition and models	106
3.5.1. Ideal solution	106
3.5.2. Excess Gibbs energy and activity coefficients	108
3.5.3. Classification of activity-coefficient models	109
3.5.4. Purely correlative Margules models	110
3.5.5. Redlich–Kister purely correlative model	112
3.5.6. The Van Laar model	113
3.5.7. The Scatchard–Hildebrand (SH) model.	115

3.5.8. The NRTL (non-random two-liquid) model with three adjustable parameters per binary system.	116
3.5.9. NRTL models with four and six adjustable parameters per binary system.	118
3.5.10. Wilson and Flory–Huggins models	118
3.5.11. UNIQUAC model.	120
3.5.12. The original UNIFAC model and its extensions	124
3.5.13. Summary: an aid to selecting an activity-coefficient model	126
3.6. Calculation of the vapor–liquid equilibrium of binary systems at low temperature and low pressure	128
3.6.1. Bubble-point pressure calculation	130
3.6.2. Calculation of the dew-point pressure.	133
3.6.3. Calculation of the bubble-point temperature	133
3.6.4. Calculation of the dew-point temperature	134
3.6.5. PT-flash calculation	135
Chapter 4. Estimation of the Thermodynamic Properties of Mixtures from an Equation of State: An Overview of Models and Calculation Procedures.	137
4.1. The phase-equilibrium condition and the ϕ - ϕ approach.	137
4.2. General presentation of the usual volumetric equations of state applicable to mixtures	138
4.3. Virial expansions	139
4.4. Cubic equations of state	140
4.4.1. Generalities	140
4.4.2. Classic mixing rules (known as “Van der Waals” mixing rules)	141
4.4.3. Advanced mixing rules by combining an equation of state with an activity-coefficient model.	147
4.4.4. Short summary of the mixing rules for cubic equations of state	157
4.5. Equations of state based on the “statistical associating fluid theory” (SAFT)	158
4.6. Specific equations of state for particular mixtures	161
4.7. Practical use of the equations of state for mixtures	161
4.7.1. What can be calculated from an equation of state for mixtures?	161
4.7.2. Calculation of mixing properties using a pressure-explicit equation of state	162
4.7.3. Calculation principle of vapor–liquid equilibrium using the ϕ - ϕ approach	165

Chapter 5. General Summary: Decision Tree to Select a Thermodynamic Model in Order to Simulate or Design a Chemical Process	169
5.1. Selection of thermodynamic models for representation of pure substances	169
5.2. Selection of thermodynamic models for representation of mixtures	172
References	177
Index	185