9 Thermodynamic Properties of Pure Fluids

9.1 Introduction

In the previous Chapter we discussed the evaluation of physical, i.e. experimentally determinable, properties of pure fluids: pressure-volume-temperature \((PVT)\) relationships and heat capacities. In this Chapter we turn to thermodynamic properties, i.e. properties that cannot be measured directly. Rather, they are determined indirectly by using relationships that express them in terms of physical properties. These thermodynamic properties are:

* internal energy
* entropy
* enthalpy
* Helmholtz free energy
* Gibbs free energy (and the associated properties: chemical potential and fugacity).

We will concentrate our attention to the most important among them for chemical engineering applications: entropy, enthalpy, and fugacity.

We must emphasize again that thermodynamic properties are not measurable quantities. They are concepts, mathematical constructs in a strict sense, created for thermodynamics; and their values are determined from experimentally measurable quantities through relationships developed by thermodynamics. Yet, these constructs are essential for the solution of everyday chemical engineering problems: from the shaft work required for the compression of a gas (entropy and enthalpy), to the design of a distillation tower (fugacity and enthalpy).
9.2 Objective and Approach

The main objective of this Chapter is to develop familiarity with the methods used for the evaluation and prediction of thermodynamic properties of pure fluids:

a. from experimental data, or
b. through estimation techniques, whenever such data are not available, which represents the typical case.

We will start with the development of the fundamental equations - the name given by J.W. Gibbs - because they contain all information needed for the complete description of the thermodynamic state of a system.

Unfortunately, the appropriate analytical expressions for the fundamental equations are not available. We turn therefore to a postulate, resulting from our empirical observations and known as the fundamental postulate, that states: The macroscopic properties of a homogeneous fluid on a molar basis can be expressed in terms of its pressure, temperature and composition.

Using this postulate, we develop a framework of expressions for the evaluation of thermodynamic properties of fluids from $PVT$ and ideal gas heat capacity data; and, since in the typical case $PVT$ data are not available, estimation techniques are emphasized.

We proceed then to discuss the concepts of chemical potential and fugacity, essential for Phase and Chemical Reaction Equilibrium calculations as we will see in later Chapters. We close with a summary of our observations on the evaluation of thermophysical properties of pure fluids.

9.3 The Fundamental Equations: Closed Systems

If we are to determine thermodynamic properties from the physical ones, the appropriate relationships between these two types of properties must be established. These relationships are referred to as fundamental equations, for they contain all the information needed for the complete description of the state of a system.

We will start our discussion with closed systems, i.e. systems that do not exchange mass with the surroundings and, consequently, their mass is constant, and then consider - in the next Section - open systems, i.e. systems of variable mass.