ChapterII: Cubic Equations of State

II.1. Introduction

An **equation of state (E-S)** links the quantities of a fluid: **pressure P, molar volume Vm** and **temperature** T.

equations **of state** are among the most widely used in thermodynamics to describe the behavior of pure fluids and mixtures.

They are called *cubic* because the expression in **molar volume Vm** leads to a **third-degree equation.**

They are essential for :

- calculate the molar volumes of liquids and vapors,
- estimate the compressibility factors Z,
- liquid-vapor equilibria (LVE),
- predict densities, pressures, enthalpies and entropies.

II. 2. General form of a cubic equation of state:

A cubic equation of state is always written in the form:

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m(V_m + b) + b(V_m - b)}$$

Or :

- a: energy parameter (molecular interaction)
- b: volumetric parameter (volume covolume / molecular repulsion)
- R: ideal gas constant

Depending on the choice of formulation of parameters a and b, different models are obtained.

II.2.1. Van der Waals equation (1873):

This is the first recorded cubic equation.

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \quad ; a = \frac{27R^2T_c^2}{64P_c} \text{ and } b = \frac{RT_c}{8P_c}$$

Features :

- A simple but imprecise model.
- just for fluids close to ideal gases,
- serves as a “fundamental” model for understanding other equations.

II.2.2. Redlich -Kwong equation (1949) :

$$P = \frac{RT}{V_m - b} - \frac{a}{T^{1/2} V_m (V_m + b)}$$

Improves the description of gases at moderate temperatures.

II.2.3. Soave - Redlich -Kwong equation (SRK, 1972):

The most used equations in chemical engineering .

$$P = \frac{RT}{V_m - b} - \frac{a(T)}{V_m (V_m + b)} \quad ; a(T) = a\,\alpha(T_r, \omega)$$

$$a = 0.42748 \frac{R^2 T_c^2}{P_c} \quad \text{and} \quad b = 0.08664 \frac{RT_c}{P_c}$$

$$\alpha = \left[1 + m\left(1 - \sqrt{T_r}\right)\right]^2 \quad \text{and} \quad m = 0.480 + 1.574\omega - 0.176\omega^2$$

Benefits

- very good for hydrocarbons,
- good compromise between simplicity and precision.
- widely used in ASPEN, PROSIM, HYSYS.

II.3. Solving the cubic equation (factor Z):

The cubic equations lead to a third-degree equation:

$$Z^3+AZ^2+BZ+C=0$$

They generally yield **3 roots** :

- **liquid** root (low Z),
- a **steam root** (high Z),
- an intermediate (non-physical) root.

Z = PV / RT

$$Z=\frac{PV}{RT}$$

- **Volume of liquids and vapors:**

For a pure fluid:

- root → **liquid**
- root → **steam**

This allows us to obtain:

- V_m molar volume liquid
- V_{mv} molar volume vapor

II.4. Scope of application of cubic equations:

Equation	Precision liquids	Vapor precision	Use
Van der Waals	weak	average	historical
RK	average	Good	gas
SRK	Good	very good	ELV hydrocarbons
Peng-Robinson	very good	excellent	petrochemicals, tanks, storage

II.5. Generalized Correlations for Calculating the Molar Volume of Saturated Liquid:

Although the molar volumes of liquids can be calculated using generalized cubic equations of state, the results are often not accurate enough.

II.5.1. Rackett 's equation (1970) :

$$V_m^{sat} = V_c . Z_c^{(1-T_r)^{2/7}}$$

An alternative form of this equation is sometimes useful:

$$Z^{sat} = \frac{P_r}{T_r} Z_c^{\left[1+(1-T_r)^{2/7}\right]}$$

The only data required are the critical constants. The results are generally accurate to within 1 or 2%.

II.5.2. Modified Rackett Equation :

$$V_L = \frac{RT_c}{P_c} Z_{RA}^{\left[1+(1-T_r)^{2/7}\right]} \qquad \text{with} : Z_{RA} = 0.29056 - 0.08775\omega$$

Example:

Calculate the molar volume of the saturated liquid of n-butane at 350 K using Rackett 's equation and the modified Rackett 's equation.

	Molar mass	ω	T_c/K	P_c/bar	Z_c	V_c $cm^3 \cdot mol^{-1}$	T_n/K
n-Butane	58.123	0.200	425.1	37.96	0.274	255.	272.7