

# CEN 202 THERMODYNAMICS, VIRIAL EQUATIONS OF STATE

## Two Forms of the Virial Equation

A useful auxiliary thermodynamic property is defined by the equation:

$$Z \equiv \frac{PV}{RT} = \frac{V}{V_{ig}}$$

This dimensionless ratio ( $Z$ ) is called the compressibility factor. It is a measure of the deviation of the real-gas molar volume from its ideal-gas value.

For the ideal-gas state,  $Z = 1$ . At moderate temperatures its value is usually  $Z < 1$ , though at elevated temperatures it may be  $Z > 1$ .

$$PV = \alpha = RT, \text{ Eq. } PV = \alpha (1 + B'P + C'P^2 + D'P^3 + \dots)$$

becomes as below:

$$Z = 1 + B'P + C'P^2 + D'P^3 + \dots$$

## Two Forms of the Virial Equation

An alternative expression for  $Z$  is also in common use:

$$Z = 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \dots \quad \left( \text{remember; } P \propto \frac{1}{V} \right)$$

Both of these equations are known as *virial expansions*, and the parameters  $B'$ ,  $C'$ ,  $D'$ , etc., and  $B$ ,  $C$ ,  $D$ , etc., are called *virial coefficients*. Parameters  $B'$  and  $B$  are *second* virial coefficients;  $C'$  and  $C$  are *third* virial coefficients, and so on. For a given gas the virial coefficients are functions of temperature only.

# CUBIC EQUATIONS OF STATE

Cubic equations are in fact the simplest equations capable of representing both liquid and vapor behavior.

## The van der Waals Equation of State

The first practical cubic equation of state was proposed by J. D. van der Waals in 1873:

$$P = \frac{RT}{V - b} - \frac{a}{V^2}$$

Here,  $a$  and  $b$  are positive constants; when they are zero, the equation is  $PV=RT$ .

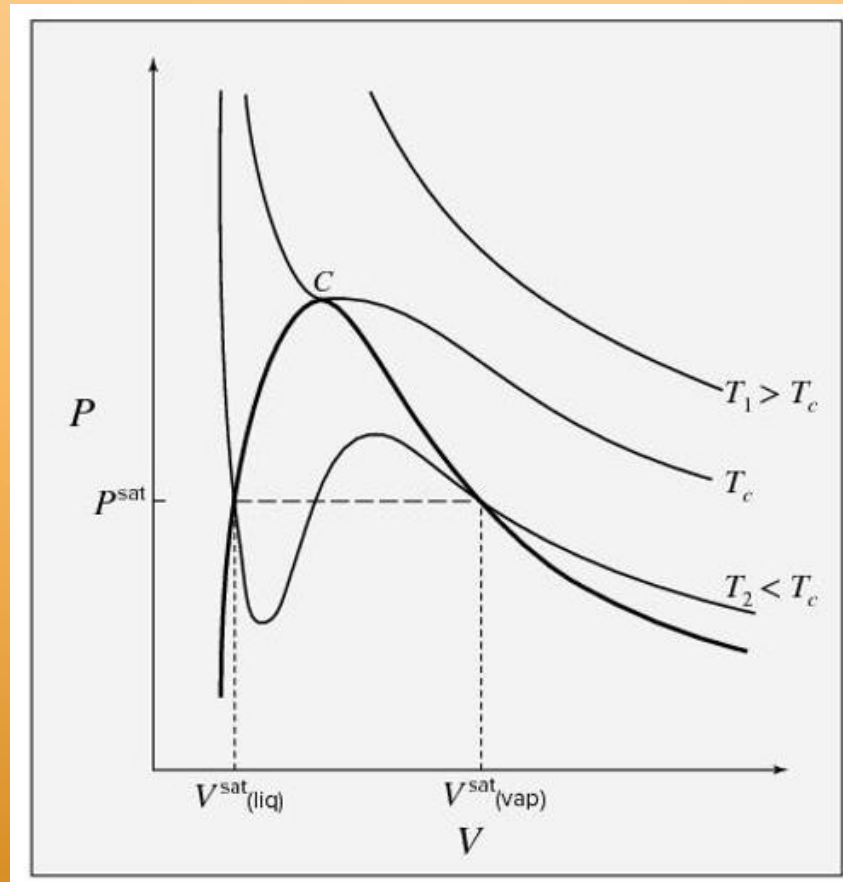
$a/V^2 \rightarrow$  related to the attractive forces between molecules (pressure).

$b \rightarrow$  related to the finite size of molecules (volume).

Given values of  $a$  and  $b$  for a particular fluid, one can calculate  $P$  as a function of  $V$  for various values of  $T$ . Figure 3.9 is a schematic PV diagram showing three such isotherms.

# CUBIC EQUATIONS OF STATE

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Text Book: : J. M. Smith, H. C. Van Ness, M. M. Abbott, M. T. Swihart. "INTRODUCTION TO CHEMICAL ENGINEERING THERMODYNAMICS", EIGHTH EDITION. 2018

# A GENERIC CUBIC EQUATION OF STATE

A mid-20th-century development of cubic equations of state was initiated in 1949 by publication of the Redlich/Kwong (RK) equation:

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

Subsequent enhancements have produced an important class of equations, represented by a *generic cubic equation of state*:

$$P = \frac{RT}{V - b} - \frac{a(T)}{(V + \epsilon b)(V + \alpha b)}$$

The assignment of appropriate parameters leads not only to the van der Waals and the Redlich/Kwong (RK) equations, but also to the Soave/Redlich/Kwong (SRK) and the Peng/Robinson (PR) equations. For a given equation,  $\epsilon$  and  $\sigma$  are pure numbers, the same for all substances, whereas parameters  $a(T)$  and  $b$  are substance dependent. The temperature dependence of  $a(T)$  is specific to each equation of state. The SRK equation is identical to the RK equation, except for the  $T$  dependence of  $a(T)$ .

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