Chemical Engineering Thermodynamics

CHE307
Chapter 3

Volumetric properties of pure fluids
Pure substance

*Pure substance* is a substance which has a fixed chemical composition throughout (like water, nitrogen, …).

A pure substance does not have to be a single chemical element or compound. A mixture of various chemical elements also qualifies as a pure substance as long as the mixture is homogeneous.

___ Volumetric properties & Equation of state ___

Thermodynamics properties as U and H are often evaluated from measurements of molar volume as a function of temperature and pressure, yielding to *Pressure/Volume/Temperature* (*PVT*) relations which may be expressed mathematically as *equation of state*.

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PVT behavior of pure substances

State 1

Heat transferred to the water at constant pressure

State 2

AT 1 atm and 20°C water exists in the liquid phase, called compressed liquid or subcooled liquid

State 3

T = 100 °C
P = 1 atm

AT 1 atm and 100°C water exists as a liquid which is ready to vaporize, called saturated liquid

State 4

As more heat is transferred, part of saturated liquid vaporizes (saturated liquid-vapor mixture)

T = 100 °C
P = 1 atm

State 5

As more heat is transferred, the T° of the vapor starts to rise (superheated vapor)

T = 300 °C
P = 1 atm

At 1 atm pressure, the T° remains ct at 100°C until the last drop of liquid is vaporized (saturated vapor)
The constant pressure phase change process described in the previous slide is illustrated on this T-v diagram.
PVT behavior of pure substances

Let us repeat the same experience at a higher pressure (1MPa). In this case, water will have a smaller specific volume than it did at 1 atm.

As heat is transferred to the water at this new pressure, the process will follow a path which looks very much like the previous one with some noticeable differences:

- Water will start boiling at a much higher temperature (180°C).
- The sp volume of the sat liquid is larger and that of the sat vapor is smaller, that is the saturation line that connects the tow saturated points is much shorter.

As the process is increased further, the saturation line will continue to get shorter and will become a point called **the critical point**.
T-v and P-v diagrams

The saturated liquid states can be connected by a line which is called the saturated liquid line.

The saturated vapor states can be connected by another line called the saturated vapor line.

These lines meet each other at the critical point, forming a dome. All the states that involve both phases in equilibrium are located under the dome which is called the saturated liquid vapor mixture region.

The P-v diagram of a pure substance is very similar to the T-v diagram, but the T constant lines on this diagram have a downward trend.

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This diagram is also called the phase diagram since all three phases are separated from each other by three lines:

- The **sublimation** line separate solid and vapor regions.
- The **vaporization** line separate vapor and liquid regions.
- The **melting (fusion)** line separate vapor and liquid regions.

These three lines meet at the triple point, where all three phases coexist in equilibrium. The vaporization line ends at the critical point because no distinction can be made between liquid and vapor phases above this point.
Extension for the solid phase and critical region
Single phase region

A relation connection P, V and T expressing analytically as \( f(P, V, T) = 0 \) describes regions where a single phase exists. Such relation is known as the \textit{PVT equation of state}.

An equation of state may be solved for any one of the three quantities P, V and T as a function of the other two. For example, \( V = f(T, P) \) and

\[
dV = \left( \frac{\partial V}{\partial T} \right)_P dT + \left( \frac{\partial V}{\partial P} \right)_T dP
\]

But, the partial derivatives in this equation have definite physical meanings:

\[
\beta = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P \quad \text{Volume expansivity}
\]

\[
\kappa = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T \quad \text{Isothermal compressibility}
\]

\[
\frac{dV}{V} = \beta \times dT - \kappa \times dP
\]
Equations of state

Virial EOS

Cubic EOS

Ideal gas

VdW
RK
SRK
PR
Virial equations of state

Isotherms for gases are relatively simple curves for which \( V \) decreases as \( P \) increases. One way to describe these isotherms is to express the product \( PV \) by a power series in \( P \):

\[
PV = a + bP + cP^2 + \cdots
\]

\[
PV = a\left(1 + B'P + C'P^2 + D'P^3 + \cdots\right)
\]

With: \( B' = \frac{b}{a} \) and \( C' = \frac{c}{a} \) etc. Where \( a, B' \) and \( C' \) are constants for a given \( T^\circ \) and given chemical species.

But, experimental studies have shown that the parameter “\( a \)” is the same function of temperature for all chemical species, and that: \( a = RT \)
Virial equations of state

Let us define an auxiliary thermodynamic property as: \[ Z = \frac{PV}{RT} \]

This dimensionless ration is called the compressibility factor.

With this definition, the Virial equation can be expressed in two forms (with \( a = RT \)):

\[
Z = 1 + B'P + C'P^2 + D'P^3 + \cdots
\]

\[
Z = 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \cdots
\]

The two sets of virial coefficients \((B, B', C, C', \ldots)\) are related as follows:

\[
B' = \frac{B}{RT} \quad C' = \frac{C - B^2}{(RT)^2} \quad D' = \frac{D - 3BC + 2B^3}{(RT)^3}
\]

Many other equations of state have been proposed for gases, but the virial equations are only ones firmly based on statistical mechanics, which provides physical significance to the virial coefficients.
The ideal gas

For an ideal gas, there is no interaction between molecules, and the virial coefficients would be zero, so:  

\[ Z = 1 \quad \text{and} \quad PV = RT \]

This is valid when the pressure approaches zero:  

\[ P \rightarrow 0 \quad \text{And so:} \quad V \rightarrow \infty \]

In this case, the internal energy is function only of the temperature  

\[ U = U(T) \]

But:  

\[ C_V = \left( \frac{dU}{dT} \right)_V = \frac{dU(T)}{dT} = C_V(T) \quad \text{So, } C_V \text{ is function of the } T^\circ \text{ only.} \]

The enthalpy is also a function of temperature only. Indeed:

\[ H = U + PV = U(T) + RT = H(T) \]

But:  

\[ C_P = \left( \frac{dH}{dT} \right)_P = \frac{dH(T)}{dT} = C_P(T) \quad \text{So, } C_P \text{ is also function of the } T^\circ \text{ only.} \]

At the same time, for an ideal gas:

\[ C_P = \frac{dH}{dT} = \frac{dU}{dT} + \frac{d(PV)}{dT} = C_V + R \]
Equations for process calculations for ideal gases

For an ideal gas, regardless of the kind of processes causing the change, $\Delta U$ and $\Delta H$ are always given by:

\[ dU = C_V dT \quad \text{or} \quad \Delta U = \int C_V dT \]

\[ dH = C_P dT \quad \text{or} \quad \Delta H = \int C_P dT \]

As we will see, ideal gas is a model fluid described by simple property relations. In process calculations, gases at pressures up to a few bars may often be considered ideal and simple equations then apply.

Expression of work:

\[ dW = -PdV = -RT \frac{dV}{V} \quad \text{because:} \quad PV = RT \]

Expression of heat:

\[ dQ = dU - dW = C_V dT - (-PdV) = C_V dT + RT \frac{dV}{V} \]
Equations for process calculations for ideal gases

\[ dW = -PdV = -RT \frac{dV}{V} \]

because \( PV = RT \)

\[ dQ = dU - dW = C_v dT - (-PdV) = C_v dT + RT \frac{dV}{V} \]

with \( V = \frac{RT}{P} \) and \( C_v = C_p - R \)

\[ dW = -RdT + RT \frac{dP}{P} \quad dQ = C_p dT - RT \frac{dP}{P} \]

with \( T = \frac{PV}{R} \) and \( C_v = C_p - R \)

\[ dW = -pdV \quad dQ = \frac{C_v}{R} VdP + \frac{C_p}{R} PdV \]
Application for various kinds of processes

Isothermal (Constant-T) process

\[ \Delta U = \Delta H = 0 \]
\[ Q = -W = RT \ln \frac{V_2}{V_1} = -RT \ln \frac{P_2}{P_1} \]

In these expressions, the implicit assumptions are that the system is closed and the process is mechanically reversible.

Isobaric (Constant-P) process

\[ \Delta U = \int C_v dT \quad \Delta H = \int C_p dT \]
\[ Q = \Delta H = \int C_p dT \quad W = -R(T_2 - T_1) \]

Isochoric (Constant-V) process

\[ \Delta U = \int C_v dT \quad \Delta H = \int C_p dT \]
\[ Q = \Delta U = \int C_v dT \quad W = -\int PdV = 0 \]
Adiabatic (Constant heat capacities) process

An adiabatic process is one for which there is no heat transfer between the system and its surroundings; i.e., \( dQ = 0 \). So:

1. \[
dQ = C_v \, dT + RT \frac{dV}{V} = 0 \quad \Rightarrow \quad \frac{dT}{T} = -\frac{R}{C_v} \frac{dV}{V} \quad \Rightarrow \quad T_2 = \left( \frac{V_1}{V_2} \right)^{R/C_v}
\]

2. \[
dQ = C_p \, dT - RT \frac{dP}{P} = 0 \quad \Rightarrow \quad \frac{dT}{T} = \frac{R}{C_p} \frac{dP}{P} \quad \Rightarrow \quad T_2 = \left( \frac{P_2}{P_1} \right)^{R/C_p}
\]

3. \[
dQ = \frac{C_v}{R} \, V \, dP + \frac{C_p}{R} \, P \, dV = 0 \quad \Rightarrow \quad \frac{dP}{P} = \frac{C_p}{C_v} \frac{dV}{V} \quad \Rightarrow \quad P_2 = \left( \frac{V_1}{V_2} \right)^{C_p/C_v}
\]
Application for various kinds of processes

Adiabatic (Constant heat capacities) process

If we put: \( \gamma = \frac{C_P}{C_V} \)  the previous equations may also be expressed as:

1. \( TV^{\gamma-1} = \text{const} \)
2. \( TP^{(1-\gamma)/\gamma} = \text{const} \)
3. \( PV^\gamma = \text{const} \)

These equations are restricted in application to ideal gases with constant heat capacities undergoing mechanically reversible adiabatic expansion or compression.

Adiabatic process  \( dQ = 0 \), so:

\[ dW = dU = C_V dT \]

For constant \( C_V \):

\[ W = \Delta U = C_V \Delta T \]

or \( C_V = \frac{R}{\gamma - 1} \)  so \( W = C_V \Delta T = \frac{R \Delta T}{\gamma - 1} \)
Application for various kinds of processes

Polytropic process

With \( d \) a constant, this process is defined as a process represented by the empirical equation:

\[
P V^\delta = \text{const}
\]

Polytropic means “turning many ways”

For specific values of \( d \), different processes could be described as shown in this figure:

- **Isobaric process**  \( \delta = 1 \)
- **Isothermal process**  \( \delta = 0 \)
- **Adiabatic process**  \( \delta = \gamma \)
- **Isochoric process**  \( \delta = \pm \infty \)
Cubic equations of state

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

The first practical cubic EOS was proposed by van der Waals in 1873:

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

“\(a\)” and “\(b\)” are positive constants. When they are zero, the ideal gas equation is recovered.

Explain in the PV diagram the occurrence of isotherms below and above the critical point and the physical meaning of each root.

(Read the last § of page 91)
A generic cubic equation of state

Since the introduction of de VdW equation, several hundred cubic EOS have been proposed. All are special cases of the equation:

\[
P = \frac{RT}{V - b} - \frac{\theta(V - \eta)}{(V - b)(V^2 + \kappa V + \lambda)}
\]

*b*, *t*, *κ*, *λ* and *η* are parameters which depend on temperature and composition.

This reduces to the VdW EOS when:

\[\eta = b \quad \theta = a \quad \kappa = \lambda = 0\]

With the assignments:

\[\eta = b \quad \theta = a(T) \quad \kappa = (\varepsilon + \sigma)b \quad \lambda = \varepsilon\sigma b^2\]

an important class of cubic equations results from these assignments:

\[
P = \frac{RT}{V - b} - \frac{a(T)}{(V + \varepsilon b)(V + \sigma b)}
\]

The temperature dependence \(a(T)\) is specific to each EOS.

VdW EOS when: \(a(T) = a \quad (\varepsilon = \sigma = 0)\)
Determination of Equation-of-State parameters

EOS parameters for a particular substance may be evaluated by a fit to available PVT data.

For cubic equation of state, suitable estimates are found from critical properties ($T_c$, $P_c$ and $V_c$), imposing the mathematical conditions:

$$
\left\{ \begin{array}{l}
\left( \frac{\partial P}{\partial V} \right)_{T;cr} = 0 \\
\left( \frac{\partial^2 P}{\partial V^2} \right)_{T;cr} = 0
\end{array} \right.
$$

Ask students to apply this procedure to estimate VdW parameters. (HW)

See the expression of the generic EOS parameters (3.45 & 3.46)
Theorem of corresponding states

Two parameter correlations

\[ Z = f(T_r, P_r) \]

Three parameter correlations

\[ Z = f(T_r, P_r, \omega) \]
Theorem of corresponding states

All fluids, when compared at the same reduced temperature and reduced pressure, have approximately the same compressibility factor. These correlations are very nearly exact for the simple fluids (Ar, Kr, Xe) but systematic deviations are observed for more complex fluids. Appreciable improvements result from introduction of a third corresponding state parameter, characteristic of molecular structure.

The most popular parameter is the acentric factor $\omega$, introduced by Pitzer and defined as:

$$\omega = -1.0 - \log\left(P_{r}^{sat}\right)_{T_r=0.7}$$

Values of $\omega$, $T_C$, $P_C$ and $V_C$ for a number of fluids are listed in App. B.

Reduced temperature $T_r = T/T_c$

Reduced pressure $P_r = P/P_c$
Theorem of corresponding states

This yields to \textit{the three parameter theorem of corresponding states}:

All fluids having the same value of $\omega$, when compared at the same $T_r$ and $P_r$, have about the same value of $Z$, and all deviate from ideal gas behavior to about the same degree.

The definition of $w$ makes its value zero for argon, krypton and xenon.

See table 3.1 for parameter assignments for the famous EOS.
Generalized correlations for gases

Pitzer correlations for the compressibility factor

\[ Z = Z^0 + \omega Z^1 \]

Where \( Z_0 \) and \( Z_1 \) are functions of both \( T_r \) and \( P_r \). So, this equation is a simple linear relation between \( Z \) and \( w \) for given \( T_r \) and \( P_r \).

When \( w = 0 \), the case for the simple fluids, \( Z_0 \) becomes identical with \( Z \).

\( Z_1 \) is a small correction of \( Z \), its omission does not introduce large errors.

The Pitzer form correlation developed by Lee and Kesler found greatest favor. It takes the form of tables given in App. E (E1 – E4)

**See App. F for interpolation**

This correlation provides reliable results for gases which are nonpolar or only slightly polar.
Generalized correlations for gases

Pitzer correlations for the second Virial coefficient

The tabular nature of the generalized compressibility factor correlation is disadvantage. Approximate analytical expression for limited range of $P$ exist.

The basis for this is the simplest form of the virial equation:

$$Z = 1 + \frac{BP}{RT} = 1 + \hat{B} \frac{P_r}{T_r} \quad \text{with} \quad \hat{B} = \frac{BP_C}{RT_C}$$

Pitzer and co. proposed a second correlation for $\hat{B}$

$$\hat{B} = B^0 + \omega B^1$$

So:

$$Z = 1 + B^0 \frac{P_r}{T_r} + \omega B^1 \frac{P_r}{T_r}$$

Comparison with: $Z = Z^0 + \omega Z^1$ gives:

$$Z^0 = 1 + B^0 \frac{P_r}{T_r} \quad \text{and} \quad Z^1 = B^1 \frac{P_r}{T_r}$$
Generalized correlations for gases

Pitzer correlations for the second Virial coefficient

As the second virial coefficient $B$, $B^0$ and $B^1$ are function of $T_r$ only.

They could be represented by the following equations:

$$B^0 = 0.083 - \frac{0.422}{T_r^{1.6}}$$
$$B^1 = 0.139 - \frac{0.172}{T_r^{4.2}}$$

This correlation has validity only at low to moderate pressures where $Z$ is linear in pressure.

In addition, it is most accurate for nonpolar species and least accurate for highly polar and associating molecules.

Example 3.10
Generalized correlations for liquids

Racket equation

Saturated liquid volumes are calculated by:

\[ V_{sat} = V_C Z_C (1-Tr)^{2/7} \]

This equation is often written in the equivalent form:

\[ Z_{sat} = \frac{P_r}{T_r} Z_C \left[ 1 + (1-Tr)^{2/7} \right] \]

This method is remarkably accurate for many substances but it underpredicts \( V_s \) when \( Z_C \) is smaller than 0.22.

Other forms exist for this equation (correlated with the acentric factor (\( \omega \)) or using a experimental density as a reference point at a given temperature).
Recommendations

To characterize small deviations from ideal behavior use the truncated virial equation (with B or B and C). Do not use this equation for liquid phases.

For normal fluids, use generalized cubic equation. Different models give equivalent and reliable results except for polar and associating substances.

For polar and associating fluids, use a method based on four or more parameters (non-discussed in this chapter). Perturbation expressions and chemical models are very accurate.

To calculate only saturated liquid volumes, use Racket correlation.