SKF2213: CHEMICAL ENGINEERING THERMODYNAMICS

Volumetric Properties of Pure Fluids

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By the end of this chapter, we would have reviewed on how to:

- determine the phases of a pure substance at specified T and P.
- understand the phase diagram (PT and PV) for pure fluid.
- apply energy balance to processes containing ideal gas.
- apply the various equations of state for PVT calculations.
- apply the various generalized PVT correlation for PVT calculations.
- apply the generalized PVT correlations developed for liquid.
- determine the specific volume (V) for two-phase system with the application of quality (x).
- *Note: This chapter mostly reviews Mass Balances, Energy Balances and Thermo 1.*

The symbols V, H, U, S, A and G refer to specific properties (unit per mol or per kg).

For example:

Unit for molar specific volume: m^3/mol

Unit for mass specific volume: m^3/kg

Degree of Freedom (F)

- $F = 2 - \pi + N$

  π is number of phase

  N is number of species
- Example:

  For a system that contains water vapor,

  $F = 2 - 1 + 1 = 2$

  So, the degree of freedom is 2.
- This means that we are free to specify 2 thermodynamics variable (e.g. T and P), and the rest of thermodynamic properties (e.g. U, H, V etc.) will depend on these two variables.

For water, $T_c = 374\ ^{o}C$, $P_c = 220$ bar

Determination of the Phase for Pure Substance

T & P			**Phase**
$T>T_c$			Gas
$T< T_c$ and $P>P_c$			Liquid
$T< T_c$ and $P< P_c$	Check boiling point	If $T>T_{bpt}$	Vapor (or Gas)
$T< T_c$ and $P< P_c$	Check boiling point	If $T< T_{bpt}$	Liquid
$T< T_c$ and $P< P_c$	Check boiling point	If $T= T_{bpt}$ or T^{sat}	Two-phase (Saturation)
$T> T_c$ and $P< P_c$			Gas
$T> T_c$ and $P> P_c$			Critical fluid

Test yourself

- Water at 1 atm and 200°C?
- Water at 200 bar and 200°C?
- Water at 90 bar and 390°C?
- Water at 240 bar and 300°C?
- Water at 1 atm and 100°C?

Boiling Point Temperature and Vapor Pressure

- Correlation is given by an Antoine Equation
- The symbol for vapor pressure is P^* or P^{sat}
- The symbol for boiling point is T_{bpt} or T^{sat}
- An example of an Antoine Equation for H_2O,

$$\log_{10} P^*(mmHg) = 7.96681 - \frac{1668.21}{T_{bpt}(^oC) + 228}$$

- This correlation can be plotted to give a chart similar to the Cox Chart

The Cox chart provide the vapor pressure vs boiling point plots for a number of species.

- From the PV diagram, we know that there are correlations between PVT for a pure substance.

- V for gas is highly dependent on T and P.

  i.e. gas is highly compressible.

- V for liquid phase, however, is almost independent of T and P.

  i.e. incompressible liquid

- The correlation for PVT is known as equation of state (EOS).

Use of PVT correlations

- Determination of one of P,V,T and n of a substance.

- Calculation of thermodynamic properties such as U, H and S. For example,

$$dH = C_p dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_P \right] dP$$

The simplest form of EOS: Ideal Gas

- For gas phase only.

$$PV = RT$$

- Valid at low pressure.
- Assume no interaction among molecules.
- From degree of freedom for one component gas system (F=2)
- We say U(T,P), H(T,P),
- But P has no effect on U and H of an ideal gas
- so we write U(T) and H(T)……remember this for pure species ideal gas!

In general,

- Ideal gas EOS is valid at low pressure.
- In many cases, gas at pressure up to several bar can be assumed as ideal gas.
- To confirm this assumption, always check compressibility factor (Z) as in *PV = ZRT.*
- For ideal gas, Z=1

Caution: At $0^{o}C$ and 100 atm

CO_2:	$Z = 0.202$	non-ideal gas
N_2:	$Z = 0.9848$	almost like ideal gas

Test yourself

Substance: H_2O

1. What is NBP or T_n?
2. What is the critical T and critical P?
3. What is vapor pressure at 120°C?
4. What is boiling point at 98.7 bar?
5. Can we use ideal gas to calculate specific volume at 120°C and 250 kPa?

Heat Capacity

$$C = \frac{dQ}{dT}$$

Energy Balance

Energy balance in a closed system.

$$\partial Q + \partial W = dU + dE_K + dE_P$$

Sign convention:

Q into (or transfer to) the system is +

W into (or done on) the system is +

Note:

Here we assume only reversible boundary work, $W = -PdV$

No motor-driven work (W_S)

Constant Volume Ideal Gas Heat Capacity (C_v^{ig})

The system is not moving.

$$\partial Q + \cancel{\partial W} = dU^{ig} + \cancel{dE_K} + \cancel{dE_P}$$

No volume change
(So no work due to
volume change (-PdV))

No change of system
elevation.

So, $$\partial Q = dU^{ig}$$

Apply definition of heat capacity for the process, $C = \frac{dQ}{dT}$

$$C_v^{ig} = \frac{dU^{ig}}{dT}$$

$$dU^{ig} = C_v^{ig} dT$$

$$\Delta U^{ig} = \int C_V^{ig} \, dT$$

Remember that U^{ig} is a function of T only, so the constant volume heat capacity for ideal gas is also a function of T only

What is enthalpy?

$$H = U + PV$$

For ideal gas,

$$H^{ig} = U^{ig} + PV^{ig}$$

Constant Pressure Ideal Gas Heat Capacity (C_p^{ig})

Differentiate the enthalpy definition:

For constant pressure

$$dH^{ig} = dU^{ig} + dPV^{ig} = dU^{ig} + PdV^{ig} + \cancel{V^{ig}dP}$$

Energy balance for ideal gas in a closed system:

$$\partial Q + \partial W = dU^{ig} + \cancel{dE_K} + \cancel{dE_P}$$

There is W due to reversible volume change (-PdV^{ig}).
For constant pressure process.

$$\partial Q - PdV^{ig} = dU^{ig}$$

$$\partial Q = dU^{ig} + PdV^{ig}$$

So, $$\partial Q = dH^{ig}$$

From definition of heat capacity,

$$C = \frac{dQ}{dT}$$

$$C_P^{ig} = \frac{dH^{ig}}{dT}$$

$$dH^{ig} = C_P^{ig} dT \qquad \Delta H^{ig} = \int C_P^{ig} \, dT$$

Remember that H^{ig} is a function of T only, so constant pressure heat capacity for ideal gas is also a function of T only as given by,

$$C_p^{ig} = R(A + BT + CT^2 + DT^{-2})$$

$$\frac{C_p^{ig}}{R} = A + BT + CT^2 + DT^{-2}$$

See **Appendix C** for constant *A, B, C, D*

Test yourself

- How to calculate ΔH^{ig}?
- How to calculate ΔU^{ig}?

Test yourself

- Show that for ideal gas,

$$C^{ig}_{p} = C^{ig}_{v} + R$$

Energy Balance for System with Ideal Gas

Isothermal Process

Energy balance for ideal gas in a closed system.

$$\partial Q + \partial W = dU^{ig} + \cancel{d}E_K + \cancel{d}E_P$$

For isothermal process ($\Delta T=0$),

$$dU^{ig}=0$$

$$\partial Q + \partial W = 0$$

$$\partial Q = -\partial W = PdV = \frac{RT}{V}dV$$

$$Q = -W = RT\ln\frac{V_2}{V_1} = -RT\ln\frac{P_2}{P_1}$$

Isobaric Process (*ΔP=0)*

Energy balance for ideal gas in a closed system,

$$\partial Q + \partial W = dU^{ig} + \cancel{dE}_K + \cancel{dE}_P$$

$$\partial Q - PdV = dU^{ig}$$

$$\partial Q = dU^{ig} + PdV = dH^{ig}$$

$$Q = \int C_P^{ig}\, dT$$

Note: Rev. boundary work,

$$\partial W = -PdV$$

$$W = -P(V_2 - V_1) = -R(T_2 - T_1)$$

Also,

$$\Delta H^{ig} = \int C_P^{ig}\, dT \qquad dH^{ig} = dU^{ig} + dPV$$

$$\Delta U^{ig} = \int C_V^{ig}\, dT \qquad dH^{ig} = dU^{ig} + PdV + V\cancel{dP}$$

Isochoric Process (*ΔV=0*)

Note,

$$\Delta H^{ig} = \int C_P^{ig}\, dT$$

$$\Delta U^{ig} = \int C_V^{ig}\, dT$$

$$\partial W = -P\cancel{dV}$$

$$W = 0$$

Energy balance:

$$\partial Q + \cancel{\partial W} = dU^{ig} + \cancel{dE}_K + \cancel{dE}_P$$

$$\partial Q = dU^{ig}$$

$$Q = \int C_v^{ig}\, dT$$

Adiabatic Process (*Q=0*)

Energy balance for ideal gas in a closed system,

$$\cancel{\partial Q} + \partial W = dU^{ig} + d\cancel{E_K} + d\cancel{E_P}$$

$$\partial W = dU^{ig}$$

$$W = C_v^{ig} \Delta T$$

$$\text{Let } \gamma = \frac{C_p^{ig}}{C_v^{ig}} = \frac{C_v^{ig} + R}{C_v^{ig}} = 1 + \frac{R}{C_v^{ig}}$$

so

$$C_v^{ig} = \frac{R}{\gamma - 1}$$

$$W = \frac{R\Delta T}{\gamma - 1} = \frac{R(T_2 - T_1)}{\gamma - 1} = \frac{P_2V_2 - P_1V_1}{\gamma - 1} \qquad \text{(eqn 3.33)}$$

Note:

$$\Delta H^{ig} = \int C_P^{ig} dT$$

$$\Delta U^{ig} = \int C_V^{ig} dT$$

$$dH^{ig} = dU^{ig} + dPV$$

$$C_p dT = C_v dT + RdT$$

…continue Adiabatic Process

Another approach:

$$\partial W = dU^{ig}$$

Rev. boundary work,

$$-PdV = C_v^{ig} dT$$

$$\frac{-RT}{V} dV = C_v^{ig} dT$$

$$\frac{-R}{C_v^{ig}} \frac{dV}{V} = \frac{dT}{T}$$

$$\frac{-R}{C_v^{ig}} \ln\frac{V_2}{V_1} = \ln\frac{T_2}{T_1}$$

$$\Delta H^{ig} = \int C_P^{ig} dT$$

$$\Delta U^{ig} = \int C_V^{ig} dT$$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\frac{R}{C_v^{ig}}}$$ we could also show that $$\frac{P_2}{P_1} = \left(\frac{V_1}{V_2}\right)^{\frac{C_P^{ig}}{C_v^{ig}}}$$ or $PV^{\gamma} = \text{constant}$

Substitute into eqn 3.33, we get rev. work

$$W = \frac{RT_1}{\gamma - 1}\left[\left(\frac{P_2}{P_1}\right)^{\frac{(\gamma-1)}{\gamma}} - 1\right]$$

Remember These!

- For any process for an ideal gas system,

$$dH^{ig} = C_P^{ig}dT \qquad \Delta H^{ig} = \int C_P^{ig}dT$$

$$dU^{ig} = C_v^{ig}dT \qquad \Delta U^{ig} = \int C_V^{ig}dT$$

- U and H are state functions (depend on T and P only)
- Q and W are path functions (depend on process path)

- For equipment producing work such as turbine

$$W_{act} = \eta W_{rev}$$

- For equipment that required work such as compressor

$$W_{act} = W_{rev}/\eta$$

where, η is efficiency

W_{act} and W_{rev} are calculated to accomplish the same change of states as the actual irreversible process.

Practice examples 3.2 to 3.7

Exercise:

One mole of nitrogen, initially at 150^oC and 8 bar, undergoes the following mechanically reversible change.

It expands isothermally to a pressure such that when it is cooled at constant volume to 50^oC its final pressure is 3 bar.

Calculate W, Q, ΔU and ΔH. If ideal gas, you can assume constant $C^{ig}_P=(7/2)R$.

To solve this,

- Draw process diagram
- Calculate for isothermal process
- Calculate for isochoric process
- Check that EB for overall process is balanced.

Single Phase Region (F=2)

- Let say $V=V(T,P)$
- Do partial derivative and then divide both sides by V,

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

$$\frac{dV}{V} = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P dT + \frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T dP$$

and let us define,

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$ as volume expansivity

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$ as isothermal compressibility

so, $$\frac{dV}{V} = \beta dT - \kappa dP$$

- This eqn is, however, mostly applicable for liquid phase calculation.

For small change of T and P, a reasonable approximation can be made if β and κ is assumed constant,

so after integration……

$$\ln\frac{V_2}{V_1}=\beta\left(T_2-T_1\right)-\kappa\left(P_2-P_1\right)$$

Note: If we assume incompressible liquid,

β and κ are 0

ΔV or $\Delta\rho$ are 0,

i.e. V and ρ are constant.

Ex 3.1b, …..see how much P increases in a rigid vessel when there is only 10^{o}C increase in T!

Generalized Correlations For Liquid Phase

1. Rackett Equation
2. Lydersen et al.

1. Rackett Equation:

Give good approximation of specific volume for saturated liquid (V^{sat}) with accuracy 1 to 2%

$$V^{sat} = V_c Z_c^{(1-T_r)^{2/7}} \quad \text{or} \quad Z^{sat} = \frac{P_r}{T_r} Z_c^{[1+(1-T_r)^{2/7}]}$$

where

$$V^{sat} = \frac{Z^{sat} RT}{P} \quad \text{and}$$

$$T_r = \frac{T}{T_c}, \quad P_r = \frac{P}{P_c}$$

2. Lydersen et al.:

This correlation provides ρ_r as a function of T_r and P_r and plotted, where

$$\rho = \rho_r \rho_c$$

or

$$V = \frac{V_c}{\rho_r}$$

Hence, for calculation of *V* for liquid

- Use correlation with β and κ
- or use Rackett Equation for V^{sat}(liq)
- or use Figure 3.16 developed by Lydersen et al.

Also, *V* is constant if assumes incompressible liquid

- Note:

  Later on we will show that cubic equation of states and Lee/Kesler correlation could also be utilized in the calculation of *V* for liquid.

Virial Equation of State

- Only for gas phase !

$$Z = \frac{PV}{RT} = 1 + B'P + C'P^2 + D'P^3 + \ldots\ldots \qquad (3.11)$$

$$Z = \frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \ldots\ldots \qquad (3.12)$$

where the relationship between the above equations are given by,

$$B' = \frac{B}{RT}$$

$$C' = \frac{C - B^2}{(RT)^2}$$

$$D' = \frac{D - 3BC + 2B^3}{(RT)^3}$$

$B^{'}, C^{'}, D^{'}, \ldots\ldots and$

$B, C, D, \ldots\ldots$ are virial coefficients

cont. Virial Equation of State

- For convenience, truncated forms are recommended for application at low to moderate pressures.
- It is suggested that for P up to 15 bar, truncation to two terms will give reasonable approximation.

$$Z = \frac{PV}{RT} = 1 + B'P$$

- Also for P up to 50 bar, truncation to three terms will give reasonable approximation.

$$Z = \frac{PV}{RT} = 1 + B'P + C'P^2$$

Cubic Equation of States

- Applicable for liquid as well as gas phase.
- The first was proposed by J.D. van der Waals in 1873.
- The van der Waals eqn,

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

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

Where,

$$a = \left(\frac{27R^2T_c^2}{64P_c}\right)$$

$$b = \frac{RT_c}{8P_c}$$

Plot P vs V for various T. We get lines such as T_2, T_C, T_1

At P and T, solving cubic equation will give three volume (*V*) roots,

- At $T=T_1$,

  One root is real and two roots are complex
- At $P=P_c$ and $T=T_c$ i.e. at critical point,

  All three roots equal to V_c
- At $T=T_2$, depending on the value of P

  i. One root is real, two roots are complex

  or

  ii. Three real roots (the actual volume root depends on P),

  Choose smallest root (liquid) if $P > P_{sat}$

  Choose largest root (gas) if $P < P_{sat}$

To determine van der Waals eqn parameters.

At critical point, the isotherm exhibits a horizontal inflection. So,

$$\left(\frac{\partial P}{\partial V}\right)_{T_c} = 0 \quad \text{and} \quad \left(\frac{\partial^2 P}{\partial V^2}\right)_{T_c} = 0$$

$$P = \frac{RT}{V-b} - \frac{a}{V^2} = RT\left(V-b\right)^{-1} - a\left(V\right)^{-2}$$

Differentiate and apply at critical point,

$$\left(\frac{\partial P}{\partial V}\right)_{T_c} = \frac{-RT_c}{\left(V_c - b\right)^2} + \frac{2a}{V_c^3} = 0 \quad \text{and} \quad \left(\frac{\partial^2 P}{\partial V^2}\right)_{T_c} = \frac{2RT_c}{\left(V_c - b\right)^3} - \frac{6a}{V_c^4} = 0$$

$$\frac{RT_c}{\left(V_c - b\right)^2} = \frac{2a}{V_c^3} \quad \text{(a)} \quad \text{and} \quad \frac{RT_c}{\left(V_c - b\right)^3} = \frac{3a}{V_c^4} \quad \text{(b)}$$

$$\frac{RT_c}{(V_c - b)^2} = \frac{2a}{V_c^3} \quad \text{(a)} \qquad \text{and} \qquad \frac{RT_c}{(V_c - b)^3} = \frac{3a}{V_c^4} \quad \text{(b)}$$

(b) $\div$ (a)

$$\frac{1}{V_c - b} = \frac{3}{2V_c}$$

$b = \frac{V_c}{3}$ subs into (a) and solve, $a = \frac{8}{9} RT_c V_c$

Substitute $a = \frac{8}{9}RT_cV_c$ and $b = \frac{V_c}{3}$ into vdW eqn,

and apply at critical point,

$$P_c = \frac{RT_c}{V_c - \frac{V_c}{3}} - \frac{\frac{8}{9}RT_cV_c}{V_c^2} = \frac{\frac{3}{8}RT_c}{V_c} \qquad so \qquad V_c = \frac{\frac{3}{8}RT_c}{P_c}$$

$$Hence \qquad a = \frac{8}{9}RT_c\frac{\frac{3}{8}RT_c}{P_c} \qquad \therefore\ a = \frac{27}{64}\frac{R^2T_c^2}{P_c}$$

$$b = \frac{\frac{\frac{3}{8}RT_c}{P_c}}{3} \qquad \therefore\ b = \frac{1}{8}\frac{RT_c}{P_c}$$

See also an equivalent but more straightforward procedure in textbook on page 93

More Cubic Equation of States

Van der Waals (1873)

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

Redlich-Kwong (1949)

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

$$a = \left(\frac{0.42748R^2T_c^{\,2}}{P_c}\right)$$

$$b = \frac{0.08664RT_c}{P_c}$$

Soave-Redlich-Kwong (1972)

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

$$\alpha = \left[1 + S(1 - T_r^{0.5})\right]^2$$

$$S = 0.48508 + 1.55171\omega - 0.15613\omega^2$$

Peng-Robinson (1976)

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

$$a = 0.45724\frac{R^2T_c^2}{P_c}$$

$$b = 0.07780\frac{RT_c}{P_c}$$

$$S = 0.37464 + 1.54226\omega - 0.26992\omega^2$$

Generic Cubic Equation of State (EOS)

- All previously mentioned cubic equation of states can be combined into a general expression known as a generic cubic equation of state

$$P = \frac{RT}{V-b} - \frac{a(T)}{(V+\varepsilon b)(V+\sigma b)} \qquad (3.42)$$

$$a(T) = \Psi \frac{\alpha(T_r) R^2 T_c^2}{P_c} \qquad (3.45)$$

$$b = \Omega \frac{RT_c}{P_c} \qquad (3.46)$$

All of the parameters are given in the textbook.

Solution to Generic Cubic EOS

For vapor & vapor-like roots,

Solution for *V*,

$$V = \frac{RT}{P} + b - \frac{a(T)}{P}\frac{V-b}{\left(V+\varepsilon b\right)\left(V+\sigma b\right)} \qquad (3.49)$$

Solution in term of *Z*,

$$Z = 1 + \beta - q\beta\frac{Z-\beta}{\left(Z+\varepsilon\beta\right)\left(Z+\sigma\beta\right)} \qquad (3.52)$$

where

$$\beta = \Omega\frac{P_r}{T_r} \text{ and } q = \frac{\Psi\alpha(T_r)}{\Omega T_r}$$

This is not volume expansivity!!

Solution by trial and error with initial guess,
for V=RT/P
or for Z=1

Solution to Generic Cubic EOS

For liquid & liquid-like roots,

Solution for *V*,

$$V = b + (V + \varepsilon b)(V + \sigma b)\left[\frac{RT + bP - VP}{a(T)}\right] \qquad (3.55)$$

Solution in term of *Z*,

$$Z = \beta + (Z + \varepsilon\beta)(Z + \sigma\beta)\frac{1 + \beta - Z}{q\beta} \qquad (3.56)$$

where

$$\beta = \Omega\frac{P_r}{T_r} \text{ and } q = \frac{\Psi\alpha(T_r)}{\Omega T_r}$$

Solution by trial and error with initial guess,

for V=b

for Z=β

Generalized Correlations for Liquid or Gas

1. Pitzer correlation for compressibility factor

1. Pitzer correlation for compressibility factor

$$Z = Z^0 + \omega Z^1 \qquad (3.57)$$

- ω is the acentric factor from Table B1

- The value of Z^0 and Z^1 are tabulated by Lee and Kesler as shown in App E table E1-E4.

Note: This correlation is also applicable for liquid phase. Numbers in the Table that are in italic are for liquid phase.

- Correlation for Z^0 is also given in Figure 3.13

- Pitzer correlation is very accurate for non-polar or slightly polar gases.

Note: Example of,

nonpolar gases: CH_4, N_2, CO_2, O_2
polar gases: NH_3, SO_2, CH_3Cl, H_2S, H_2O, NO_2

Generalized Correlations for Gases

1. Pitzer Correlations for the Second Virial Coefficient
2. Pitzer Correlations for the Third Virial Coefficient

1. Pitzer Correlations for the Second Virial Coefficient

Virial Eqn truncated after 2 terms,

$$Z = 1 + B'P = 1 + \frac{BP}{RT} = 1 + \frac{BP_c}{RT_c}\left(\frac{P_r}{T_r}\right) = 1 + \hat{B}\frac{P_r}{T_r} \qquad (3.61)$$

Pitzer correlation for second virial coefficient,

$$\hat{B} = B^0 + \omega B^1 \qquad (3.63)$$

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

So Virial Eqn with Pitzer Correlation,

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

2. Pitzer Correlations for the Third Virial Coefficient

Virial Eqn truncated after 3 terms (note: the eqn is cubic),

$$Z = 1 + \frac{B}{V} + \frac{\mathrm{C}}{\mathrm{V}^2} \qquad (3.40) \qquad\qquad Z = 1 + \hat{B}\frac{P_r}{T_r Z} + \hat{C}\left(\frac{P_r}{T_r Z}\right)^2 \qquad (3.68)$$

Pitzer correlation for third virial coefficient,

$$\hat{C} = C^0 + \omega C^1 \qquad (3.69)$$

$$C^0 = 0.01407 + \frac{0.02432}{T_r} - \frac{0.00313}{T_r^{10.5}} \quad \text{and} \quad C^1 = -0.02676 + \frac{0.05539}{T_r^{2.7}} - \frac{0.00242}{T_r^{10.5}}$$

So Virial Eqn with Pitzer Correlation,

$$Z = 1 + B^0\frac{P_r}{T_r} + \omega B^1\frac{P_r}{T_r} + \left(C^0\right)\left(\frac{P_r}{T_r Z}\right)^2 + \omega\left(C^1\right)\left(\frac{P_r}{T_r Z}\right)^2$$

Need more information….

- **Bruce E. Poling, John M. Prausnitz, John P. O' Connell, The Properties of Gases and Liquids, Fifth Edition,** McGraw Hill, 2001

Reference

Smith J.M., Van Ness H.C. , and Abbott M. M. , Introduction to Chemical Engineering Thermodynamics, 7th Edition, McGraw Hill, New York, 2001.