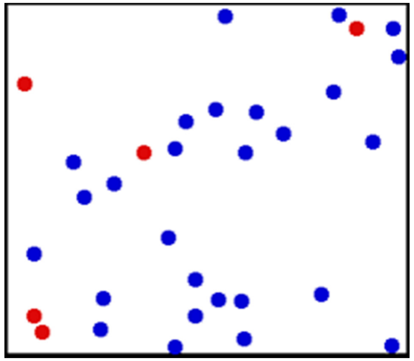
Chapter 5



Single Phase System

PVT Relationship

- Density and Specific Volume of gas do not change with pressure and temperature
- For Gas we need to know the ***PVT*** relationship
  - Pressure
  - Temperature
  - Specific Volume
- Examples of problem requiring ***PVT*** relationship
  - Propane at 120°C and 2.3 bars passes through flow meter that reads 250 L/min. What is the mass flow rate of the gas?
  - A pure hydrocarbon gas fills a 2-liter vessel at 30°C with an absolute pressure of 25 atm. How many moles of gas are contained in the vessel?
  - Calculate the volume in liters occupied by 100g of N_2 at 23°C and 3 psig.

Ideal Gas Law

- ***Equation of state*** relates the quantity (mass or moles) and volume of gas with temperature and pressure
- The simplest and mostly used is ***ideal gas law***

$$PV = nRT \quad or \quad P\dot{V} = \dot{n}RT$$

P = absolute pressure of the gas
V = volume or volumetric flow rate of gas
n = number of moles or molar flow rate of the gas
R = the gas constant
T = absolute temperature of gas

- Generally applicable at low pressure (< 1 atm) and temperature > 0°C.

Ideal Gas Law

- The equation can also be written as

$$P\hat{V} = RT$$

where $\hat{V}$ = **V/n** is the molar volume of the gas

- Any gas is presented by the above equation is known as an **ideal gas** or **perfect gas**
- 1 mol of ideal gas at 0°C and 1 atm occupies 22.415 L, whether the gas is argon, nitrogen, or any other single species or mixture of gases

Q1 - Application of Ideal Gas Law

Propane at 120°C and 1 bar absolute passes through a flow meter that reads 250 L/min. What is the mass flow rate of the gas?

How many ways can we calculate the mass flow rate? What additional information is needed?

…. Using ideal gas law

Standard Conditions for gases

- Using ***PVT*** equation is easy, provided you have a set of ***R*** constant value with different units.
- A way to avoid this is by dividing the gas law from process condition with given chosen reference condition

$$\frac{PV}{P_sV_s} = \frac{nT}{n_sT_s} \quad or \quad \frac{PV}{P_s\hat{V}_s} = n\frac{T}{T_s}$$

Standard Conditions for gases

System	T_s	P_s	V_s	n_s
SI	273 K	1 atm	0.022415 m^3	1 mol
CSS	273 K	1 atm	22.415 L	1 mol
American	492°R	1 atm	359.05 ft^3	1 lb-mole

Standard Temperature and Pressure (STP)

- Reference temperature (0°C, 273K, 32°F and 492°R) and pressure (1 atm) are commonly known as ***STP (standard temperature and pressure)***
- The other related values is easy to commit to memory like the relation of

$$\hat{V}_s = \frac{V_s}{n_s} = 0.0224\frac{\text{m}^3\text{(STP)}}{\text{mol}} \Leftrightarrow 22.4\frac{\text{liters(STP)}}{\text{mol}} \Leftrightarrow 359\frac{\text{ft}^3\text{(STP)}}{\text{lb}-\text{mole}}$$

Standard cubic meters (SCM) → m^3(STP)
Standard cubic feet (SCF) → ft^3(STP)

Q2 - Conversion from Standard Conditions (STP)

The pressure gauge on a 20 m^3 of nitrogen at 25°C reads 10 bar. Estimate the mass of nitrogen in the tank by

(i) direct solution of the ideal gas equation of state and,
(ii) conversion from standard conditions.

What does pressure reading obtained from a pressure gauge reading indicate?

The pressure gauge on a 20 m^3 of nitrogen at 25°C reads 10 bar. Estimate the mass of nitrogen in the tank by

Pressure gauge reading is not absolute pressure, i.e. P_g.
Thus, absolute pressure, $P_a = P_g + P_{atm}$

(i) direct solution of the ideal gas equation of state

(ii) conversion from standard conditions.

Effect of Temperature and Pressure on Ideal Gases

- If the input and output streams at indicated temperatures and pressures can be reasonably assumed to follow ideal gas behaviour, then

$$P_1V_1 = nRT_1 \quad and \quad P_2V_2 = nRT_2$$

$$\therefore \quad \frac{P_1V_1}{P_2V_2} = \frac{T_1}{T_2}$$

Q3 - Standard and True Volumetric Flow Rates

The volumetric flow rate of an ideal gas is given as 35.8 SCMH (i.e m^3/h at STP).

(i) Calculate the molar flow rate (mol/h),
(ii) If the temperature and pressure of the gas are 30°C and 152 kPa, calculate the actual volumetric flow rate.

(i) Molar flow (mol/h) at STP

(ii) If the temperature and pressure of the gas are 30°C and 152 kPa, calculate the actual volumetric flow rate,

Ideal Gas Mixtures - Dalton Law

- Suppose n_A moles of substance *A*, n_B moles of *B* and n_C moles of *C* and so on, are contained in a volume *V* at temperature *T* and total pressure *P*.
- The partial pressure p_A of *A* in the mixture is defined as the pressure exerted by n_A moles of *A* alone occupied at the same total volume V only for ideal gases at the same temperature *T*

From ideal gas law : $PV = nRT$ .... (1)

From partial pressure: $p_A V = n_A RT$ .... (2)

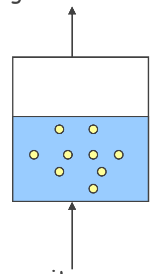
Dividing Eq. (1) by Eq. (2) : $\frac{p_A}{P} = \frac{n_A}{n} = y_A$ or $p_A = y_A P$

Thus, the ideal partial pressure of ideal gas add up to the total pressure P

$$\Sigma p_i = p_A + p_B + p_C + \ldots = (y_A + y_B + y_C + \ldots)P = P$$

Q 4 – Dalton Law

Nitrogen from a cylinder is bubbled through liquid acetone at 1.1 bar and stream 60°C at the rate of 2×10^{-4} m^3/min. The nitrogen saturated with acetone vapor leaves at 1.01325 bar, 35°C at the rate of 3.83×10^{-4} m^3/min. What is the partial pressure of acetone ? Solubility of nitrogen in liquid acetone is negligible.



Nitrogen from a cylinder is bubbled through liquid acetone at 1.1 bar and stream 60°C at the rate of 2×10^{-4} m^3/min.

The nitrogen saturated with acetone vapor leaves at 1.01325 bar, 35°C at the rate of 3.83×10^{-4} m^3/min.

What is the partial pressure of acetone ?

Ideal Gas Mixture - Amagat Law

- Suppose n_A moles of substance *A*, n_B moles of *B* and n_C moles of *C* and so on, are contained in a volume *V* at temperature *T* and total pressure *P*.
- The partial volume v_A of *A* in the mixture is defined as the volume that would be occupied by n_A moles of *A* alone only for ideal gases at the total pressure *P* at the same temperature *T* of the mixture

From ideal gas law : $PV = nRT$ .... (1)

From partial pressure: $Pv_A = n_A RT$ .... (2)

Dividing Eq. (1) by Eq. (2) : $\frac{v_A}{V} = \frac{n_A}{n} = y_A$ or $v_A = y_A V$

Thus the ideal partial volume of ideal gas add up to the total volume V :

$$v_A + v_B + v_C + \ldots = (y_A + y_B + y_C + \ldots)V = V$$

The volume fraction of a substance in an ideal gas mixture equals the mole fraction of this substance

Q5 - Ideal Gas Mixture

An ideal gas mixture contains 35% helium, 20% methane and 45% nitrogen by volume at 2.00 atm absolute and 90°C. Calculate

(a) the partial pressure of each component.

(b) the average molecular weight of the gas.

Real Gases

- At extremely low temperature or sufficiently high pressure, a value of $\hat{V}$ predicted with the ideal gas law becomes significantly inaccurate, especially when the gas contains a mixture of several gas species.
- Equation of state (EOS) for real (i.e. non-ideal or imperfect) gases

Single gas species

- Virial EOS (Benedict-Webb-Rubin, BWR)
- Cubic EOS (Soave-Redlich-Kwong, SRK)
- Compressibility Factor EOS ($PV = znRT$)

Gas mixtures

- Kay's Rule

Critical Temperature and Pressure

- Critical temperature (T_c) – the highest temperature at which a species can coexist in two phases (liquid and vapor)
- Critical pressure (P_c) – the pressure at which a species can coexist in two phases (liquid and vapor) at the critical temperature.
- A substance at T_c and P_c is said to be at its critical state
- Substances at temperatures above T_c and P_c are referred to as supercritical fluids

Physical properties for calculations involving Real Gases

	Molar mass	ω	T_c/K	P_c/bar	Z_c	V_c cm^3 mol^{-1}	T_n/K
Methane	16.043	0.012	190.6	45.99	0.286	98.6	111.4
Ethane	30.070	0.100	305.3	48.72	0.279	145.5	184.6
Propane	44.097	0.152	369.8	42.48	0.276	200.0	231.1
n-Butane	58.123	0.200	425.1	37.96	0.274	255.	272.7
n-Pentane	72.150	0.252	469.7	33.70	0.270	313.	309.2
n-Hexane	86.177	0.301	507.6	30.25	0.266	371.	341.9
n-Heptane	100.204	0.350	540.2	27.40	0.261	428.	371.6
n-Octane	114.231	0.400	568.7	24.90	0.256	486.	398.8
n-Nonane	128.258	0.444	594.6	22.90	0.252	544.	424.0
n-Decane	142.285	0.492	617.7	21.10	0.247	600.	447.3
Isobutane	58.123	0.181	408.1	36.48	0.282	262.7	261.4
Isooctane	114.231	0.302	544.0	25.68	0.266	468.	372.4
Cyclopentane	70.134	0.196	511.8	45.02	0.273	258.	322.4
Cyclohexane	84.161	0.210	553.6	40.73	0.273	308.	353.9
Methylcyclopentane	84.161	0.230	532.8	37.85	0.272	319.	345.0
Methylcyclohexane	98.188	0.235	572.2	34.71	0.269	368.	374.1
Ethylene	28.054	0.087	282.3	50.40	0.281	131.	169.4
Propylene	42.081	0.140	365.6	46.65	0.289	188.4	225.5
1-Butene	56.108	0.191	420.0	40.43	0.277	239.3	266.9
cis-2-Butene	56.108	0.205	435.6	42.43	0.273	233.8	276.9
trans-2-Butene	56.108	0.218	428.6	41.00	0.275	237.7	274.0
1-Hexene	84.161	0.280	504.0	31.40	0.265	354.	336.3
Isobutylene	56.108	0.194	417.9	40.00	0.275	238.9	266.3
1,3-Butadiene	54.092	0.190	425.2	42.77	0.267	220.4	268.7
Cyclohexene	82.145	0.212	560.4	43.50	0.272	291.	356.1
Acetylene	26.038	0.187	308.3	61.39	0.271	113.	189.4
Benzene	78.114	0.210	562.2	48.98	0.271	259.	353.2
Toluene	92.141	0.262	591.8	41.06	0.264	316.	383.8
Ethylbenzene	106.167	0.303	617.2	36.06	0.263	374.	409.4
Cumene	120.194	0.326	631.1	32.09	0.261	427.	425.6
o-Xylene	106.167	0.310	630.3	37.34	0.263	369.	417.6
m-Xylene	106.167	0.326	617.1	35.36	0.259	376.	412.3
p-Xylene	106.167	0.322	616.2	35.11	0.260	379.	411.5
Styrene	104.152	0.297	636.0	38.40	0.256	352.	418.3
Naphthalene	128.174	0.302	748.4	40.51	0.269	413.	
Biphenyl	154.211	0.365	789.3	38.50	0.295	502.	528.2
Formaldehyde	30.026	0.282	408.0	65.90	0.223	115.	254.1
Acetaldehyde	44.053	0.291	466.0	55.50	0.221	154.	294.0
Methyl acetate	74.079	0.331	506.6	47.50	0.257	228.	330.1
Ethyl acetate	88.106	0.366	523.3	38.80	0.255	286.	350.2
Acetone	58.080	0.307	508.2	47.01	0.233	209.	329.4
Methyl ethyl ketone	72.107	0.323	535.5	41.50	0.249	267.	352.8
Diethyl ether	74.123	0.281	466.7	36.40	0.263	280.	307.6
Methyl *t*-butyl ether	88.150	0.266	497.1	34.30	0.273	329.	328.4

Physical properties for calculations involving Real Gases

	Molar mass	ω	T_c/K	P_c/bar	Z_c	V_c cm^3 mol^{-1}	T_n/K
Methanol	32.042	0.564	512.6	80.97	0.224	118.	337.9
Ethanol	46.069	0.645	513.9	61.48	0.240	167.	351.4
1-Propanol	60.096	0.622	536.8	51.75	0.254	219.	370.4
1-Butanol	74.123	0.594	563.1	44.23	0.260	275.	390.8
1-Hexanol	102.177	0.579	611.4	35.10	0.263	381.	430.6
2-Propanol	60.096	0.668	508.3	47.62	0.248	220.	355.4
Phenol	94.113	0.444	694.3	61.30	0.243	229.	455.0
Ethylene glycol	62.068	0.487	719.7	77.00	0.246	191.0	470.5
Acetic acid	60.053	0.467	592.0	57.86	0.211	179.7	391.1
n-Butyric acid	88.106	0.681	615.7	40.64	0.232	291.7	436.4
Benzoic acid	122.123	0.603	751.0	44.70	0.246	344.	522.4
Acetonitrile	41.053	0.338	545.5	48.30	0.184	173.	354.8
Methylamine	31.057	0.281	430.1	74.60	0.321	154.	266.8
Ethylamine	45.084	0.285	456.2	56.20	0.307	207.	289.7
Nitromethane	61.040	0.348	588.2	63.10	0.223	173.	374.4
Carbon tetrachloride	153.822	0.193	556.4	45.60	0.272	276.	349.8
Chloroform	119.377	0.222	536.4	54.72	0.293	239.	334.3
Dichloromethane	84.932	0.199	510.0	60.80	0.265	185.	312.9
Methyl chloride	50.488	0.153	416.3	66.80	0.276	143.	249.1
Ethyl chloride	64.514	0.190	460.4	52.70	0.275	200.	285.4
Chlorobenzene	112.558	0.250	632.4	45.20	0.265	308.	404.9
Tetrafluoroethane	102.030	0.327	374.2	40.60	0.258	198.0	247.1
Argon	39.948	0.000	150.9	48.98	0.291	74.6	87.3
Krypton	83.800	0.000	209.4	55.02	0.288	91.2	119.8
Xenon	131.30	0.000	289.7	58.40	0.286	118.0	165.0
Helium 4	4.003	−0.390	5.2	2.28	0.302	57.3	4.2
Hydrogen	2.016	−0.216	33.19	13.13	0.305	64.1	20.4
Oxygen	31.999	0.022	154.6	50.43	0.288	73.4	90.2
Nitrogen	28.014	0.038	126.2	34.00	0.289	89.2	77.3
Air†	28.851	0.035	132.2	37.45	0.289	84.8	
Chlorine	70.905	0.069	417.2	77.10	0.265	124.	239.1
Carbon monoxide	28.010	0.048	132.9	34.99	0.299	93.4	81.7
Carbon dioxide	44.010	0.224	304.2	73.83	0.274	94.0	
Carbon disulfide	76.143	0.111	552.0	79.00	0.275	160.	319.4
Hydrogen sulfide	34.082	0.094	373.5	89.63	0.284	98.5	212.8
Sulfur dioxide	64.065	0.245	430.8	78.84	0.269	122.	263.1
Sulfur trioxide	80.064	0.424	490.9	82.10	0.255	127.	317.9
Nitric oxide (NO)	30.006	0.583	180.2	64.80	0.251	58.0	121.4
Nitrous oxide (N_2O)	44.013	0.141	309.6	72.45	0.274	97.4	184.7
Hydrogen chloride	36.461	0.132	324.7	83.10	0.249	81.	188.2
Hydrogen cyanide	27.026	0.410	456.7	53.90	0.197	139.	298.9
Water	18.015	0.345	647.1	220.55	0.229	55.9	373.2
Ammonia	17.031	0.253	405.7	112.80	0.242	72.5	239.7
Nitric acid	63.013	0.714	520.0	68.90	0.231	145.	356.2
Sulfuric acid	98.080	...	924.0	64.00	0.147	177.	610.0

†Pseudoparameters for $y_{N_2} = 0.79$ and $y_{O_2} = 0.21$. See Eqs. (6.88)–(6.90).

Compressibility Factor Equation of State

- An equation of state that retains the simplicity of the ideal gas law but describe the *PVT* behavior of real gas

$$PV = znRT \quad or \quad P\hat{V} = zRT$$

- The coefficient *z* is called the *compressibility factor*, and the equation is known as the *compressibility factor equation of state*
- A value of $z = 1$ correspond to ideal gas behavior
- The compressibility factor of a gas depends on the gas temperature and pressure
- Values of $z(T,P)$ for air, argon, CO_2, CO, H_2, CH_4, N_2, O_2 are given in *Perry's Chemical Engineers' Handbook*, pp 3-112 to 3-118

Corresponding States Approach for Compressibility Factors

- Simple (two-parameter) corresponding states: All fluids obey the same equation of state written in reduced form.

$$\frac{z}{z_C} = f\left(\frac{T}{T_C}, \frac{P}{P_C}\right)$$

$$z_r = f(T_r, P_r)$$

- Since z_C is nearly a constant for many organic species (about 0.27), the most often used form is

$$z = f(T_r, P_r)$$ (see charts on pp. 208-211)

Estimation of Compressibility Factors

1. All temperatures and pressures used to estimate the compressibility factor (z) must be absolute !!!!
2. Look up or estimate the critical temperature (T_c) and critical pressure (P_c)
3. If the gas is hydrogen or helium, determine the pseudo critical constant from the empirical formulas (newton's correction)

   $(T_c)_{adjusted} = T_c + 8$ K and $(P_c)_{adjusted} = P_c + 8$ atm

4. If both temperature and pressure are known
   - Calculate the reduced temperature, $T_r = T/T_c$ and reduced pressure, $P_r = P/P_c$
   - Look up the value of z on a generalized compressibility chart (*z vs P_r for specific values of T_r*)

Estimation of Compressibility Factors

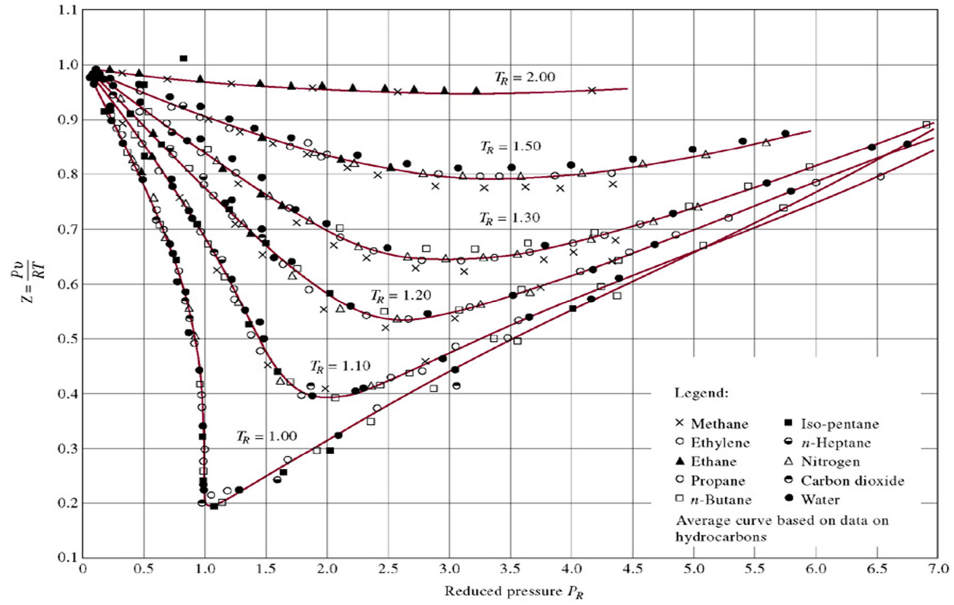
5. If either temperature or pressure and molar volume is unknown

- Calculate the ideal critical volume

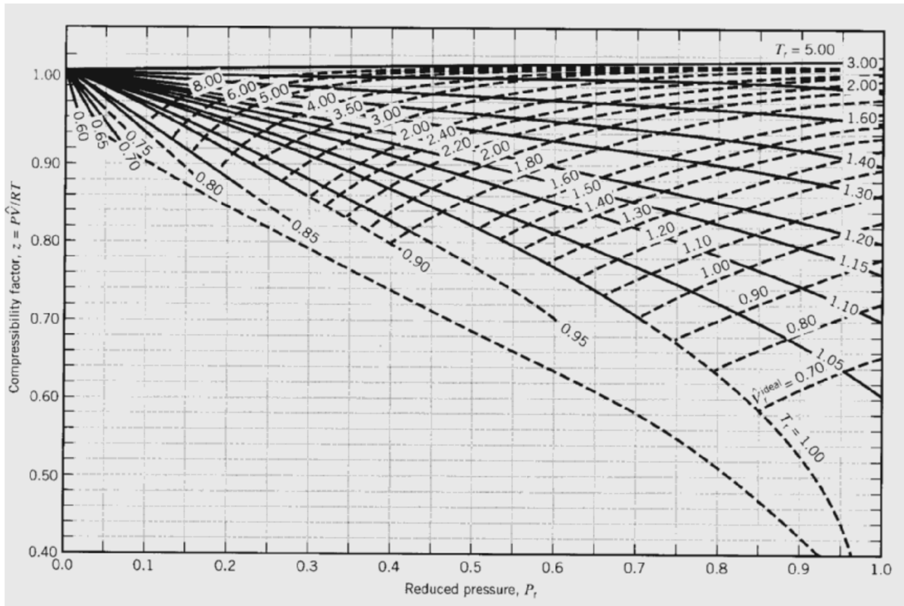
$$V_r^{ideal} = \frac{\hat{V}}{\hat{V}_c^{ideal}} = \frac{\hat{V}}{RT_c/P_c} = \frac{\hat{V}P_c}{RT_c}$$

- Look up the value of z on generalized compressibility charts (low, medium or high pressure ; z vs V_r^{ideal} for specific values of T_r)

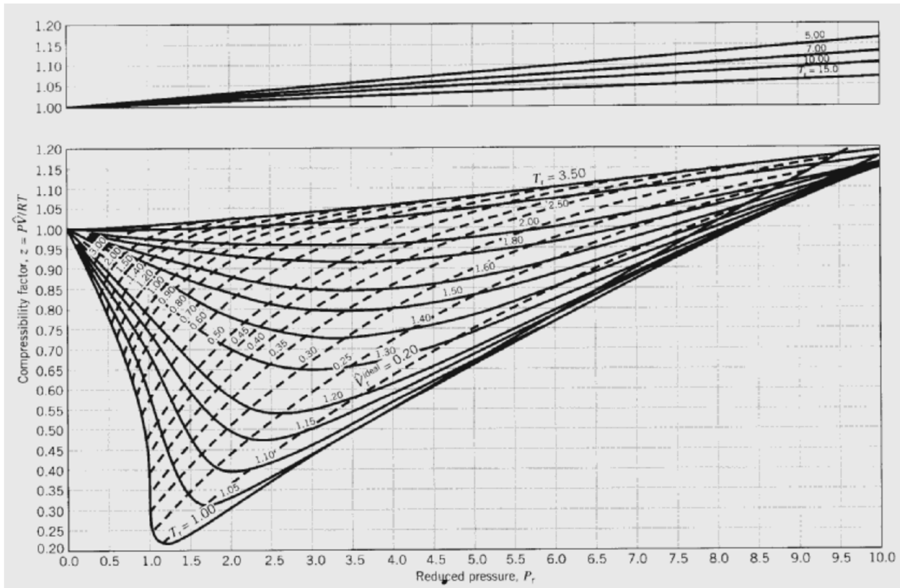
Compressibility Factor



Compressibility Factor (Low Pressures)

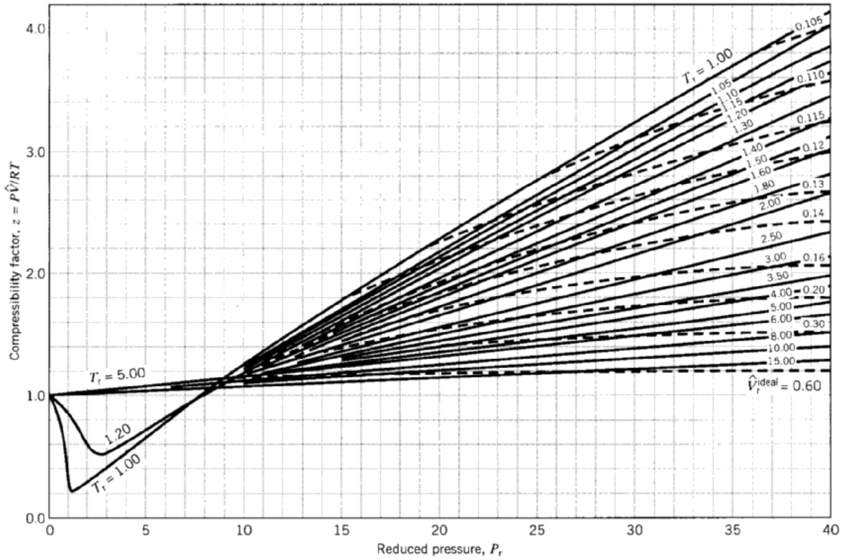


Compressibility Factor (Medium Pressures)



(Figure 5.4.3)

Compressibility Factor (High Pressures)



(Figure 5.4.4)

Q6 – Ideal Gas vs Real Gas

Natural gas contains mainly methane is stored in a 35-liter CNG tank at 3000 psig and 30°C. Estimate the actual capacity (m^3) at standard temperature and pressure (STP) assuming

a. ideal gas behaviour

b. real gas behaviour

Real Gas Mixtures: Kay's Rule

- Techniques to be used when we have mixture of real gas

$PV = z_m nRT$ *or* $P\hat{V} = z_m RT$

- Calculate the pseudo critical constant of gas mixture component
  - *Pseudo critical Temperature*: $T_c' = y_a T_{ca} + y_b T_{cb} + y_c T_{cc} + \ldots$
  - *Pseudo critical Pressure*: $P_c' = y_a P_{ca} + y_b P_{cb} + y_c P_{cc} + \ldots$
- If the temperature and pressure of the mixture are known, calculate
  - *Pseudoreduced Temperature*: $T_r' = T/T_c'$
  - *Pseudoreduced Pressure*: $P_r' = P/P_c'$
  - *Use the generalized compressibility chart to obtain z_m*
- All pseudo critical constant of mixture are simply empirical parameters and do not have any physical significance

Q7 - Kay's Rule

The interest in natural gas as an alternative fuel stems mainly from its cleaner burning qualities. Natural gas can either be stored onboard a vehicle as compressed natural gas (CNG) or natural gas (LNG). Suppose that natural gas containing 85% methane and 15% ethane by volume is stored in a 35-liter CNG tank at 3000 psig and 30°C.

a. Estimate the actual capacity (m^3) of natural gas at standard temperature and pressure (STP).
b. Calculate the exact volume (m^3) of combustion air at standard temperature and pressure (STP), if natural gas undergoes complete combustion.

Working sessions

(a) Use generalized compressibility chart to estimate z for (a) nitrogen at 40°C and 40 MPa, and (b) helium at -200°C and 350 atm.

(b) Question 5.74 (pp. 234)