Chemical Process Calculations CL204
Module-2
Properties of Gas, Vapor, and Liquid

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Module – 2

Ideal gas law :

Ideal gas: Assumptions (gas molecules).

i) do not occupy any space; infinitesimally small.

ii) No attractive forces exist between the molecules; move completely independent eachother.

iii) Molecules move randomly, straight line motion.; elastic perfectly.

molecule - molecule
" - wall.

Valid at low pressure and/or high temperature

∴ P ↑

molecules closely spaced.
ideal gas law will not valid for a real gas.

P ↑ & T ↑.

∴ $P \propto T$ when V is constant.

$P \propto \frac{1}{V}$ " T is constant. isothermal compression or expansion.

$P \propto n$., V, T are constant).

∴ $PV = nRT$ (ideal gas law). R = universal gas constant.

P = Absolute pressure of the gas, Pa, N/m^2

V = total volume occupied be the gas., m^3

n = number of moles. of the gas., kmol

T = absolute temperature of the gas, K.

$\therefore \quad \frac{V}{n}$ = volume of the gas /kmol.

$\hat{V}$ = molar volume, m^3/kgmol (MKS).

ϑ or $\hat{V}$ molar volume.

standard state system	T	P	$\hat{V}$ or ϑ
SI	273.15 K	101.325 kPa	22.415 m^3/kgmol.
universal scientific	0°C	760 mmHg	22.415 liters/gmol.
Natural gas industry	59.0°F (15°C).	14.696 psia (101.325 kPa).	379.4 ft^3/lb-mol.
American engineering unit	491.67°R (32°F)	1 atm	359.05 ft^3/lb-mol

calculate volume occupied by 40 kg CO_2 at standard state condition. (ideal gas assumed.)

$$\therefore \quad P\hat{V} = RT.$$

$$\frac{40 \text{ kg } CO_2}{} \bigg| \frac{1 \text{ kgmol } CO_2}{44 \text{ kg } CO_2} \bigg| \frac{22.415 \text{ m}^3 \, CO_2}{1 \text{ kgmol } CO_2}$$

$$= \frac{40}{44} \times \hat{V} = \text{volume occupied.}$$

$$= 20.4 \text{ m}^3 \text{ of } CO_2 .$$

other way. $P\hat{V} = RT$. — put R value in exact unit $= \underline{8.314}$ $\left(\frac{m^3 \, kPa}{K\text{-}(kgmol)}\right)$

$$101.325 \times \hat{V} = R \times 273.15 .$$

$$\hat{V} = \frac{R \times 273.15}{101.325} \quad (m^3/kmol)$$

$$\hat{V} = 22.415 \ m^3/kgmol.$$

Calculation of R. standard state

$P = 1$ atm

$\hat{V} = 22415\ cm^3/gmol.$

$T = 273.15\ K$

$22.415\ m^3/kmol$

$22.415 \times \frac{10^6}{1000}\ \frac{cm^3}{gmol.}$

$= 22415\ cm^3/gmol$

$$R = \frac{P\hat{V}}{T} = \frac{1 \times 22415}{273.15}\left(\frac{cm^3\ atm}{K \cdot gm\text{-}mol}\right)$$

$$= 82.06\ \frac{cm^3\ atm}{K \cdot gm\text{-}mol}.$$

$$R = 8.314\ \frac{kPa.m^3}{kgmol \cdot K}$$

SI

$$R = 8314.45\ \frac{Pa.m^3}{kgmol.K}$$

atm.cm^3/(mol.K) : 82.057338

atm.ft^3/(lbmol.K) : 1.31443

atm.ft^3/(lbmol.°R) : 0.73024

atm.l/(mol.K) : 0.082057338

bar.cm^3/(mol.K) : 83.144598

bar.l/(mol.K) : 0.083144598

Btu/(lbmol.°R) : 1.9872036

cal/(mol.K) : 1.9859

erg/(mol.K) : 83144598

hp.h/(lbmol.°R) : 0.0007805

inHg.ft^3/(lbmol.°R) : 21.85

– SI **J/(mol.K) : 8.3144598**

– SI **kJ/(kmol.K) : 8.3144598**

J/(kmol.K) : 8314.472

(kgf/cm^2).l/(mol.K) : 0.084784

kPa.cm^3/(mol.K) : 8314.4598

kWh/(lbmol.°R) : 0.000582

lbf.ft/(lbmol.°R) : 1545.349

mmHg.ft^3/(lbmol.K) : 999

mmHg.ft^3/(lbmol.°R) : 555

mmHg.l/(mol.K) : 62.363577

Pa.m^3/(mol.K) : 8.3144598

psf.ft^3/(lbmol.°R) : 1545.3465

calculation of density

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

$$\hat{V} = \frac{MW}{\rho} = \frac{RT}{P}$$

$$= \frac{MW}{kg/m^3}$$

$$= \frac{m^3}{\frac{kg}{MW}} = \frac{m^3}{kg\ mol}$$

$$\rho = \frac{P \times MW}{RT} = \frac{MW}{\hat{V}}$$

$$sp\ gr = \frac{\rho_A}{\underset{\text{reference sample}}{\rho_B}} = \frac{Mol\ wt_A}{Mol\ wt_B}\left(\frac{T_B}{T_A}\right) \times \left(\frac{P_A}{P_B}\right)$$

CO_2 MW = 44 , $\hat{V} = 22.415\ m^3/kg\ mol$.

$$\rho_{CO_2}\Big| = \frac{44}{22.415}\ kg/m^3 = \frac{M.W}{\hat{V}}$$

standard state
0°C / 273.15°C
101.325 kPa.

$= 1.96\ kg/m^3$

Find density of CO_2 at 27°C and at 201.325 kPa = 2 bar.

$$P\hat{V} = RT \qquad - \frac{kPa\ m^3}{kg\,mol\text{-}K}$$

$$\hat{V} = \frac{RT}{P} = \frac{8.31445 \times (27 + 273.15)}{201.325}\ \frac{m^3}{kg\,mol}$$

$$\hat{V} = 12.395\ \frac{m^3}{kg\ mol}$$

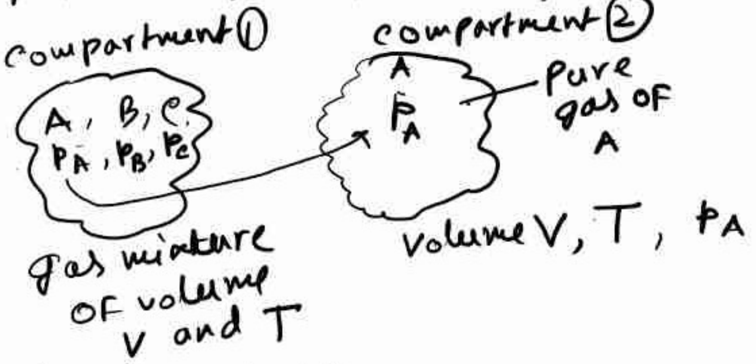
$$\rho\Big|_{CO_2\ T = 27°C + 201.325} = \frac{M.W}{\hat{V}}$$

$$= \frac{44}{12.395}\ \frac{kg}{m^3}$$

$$= 3.549\ kg/m^3$$

Ideal gas mixtures and partial pressure.

Partial pressure of Dalton, p_i, namely the pressure that would exerted by a single component in a gaseous mixture if it is existed alone in the same volume as that occupied by the mixture at the same temperature of the mixture,



$$P_{total} = p_A + p_B + p_C.$$

$$p_i V = n_i R T \quad \text{(2nd compartment)}.$$

$$P_{total} V = n_{total} R T \quad \text{(1st compartment)}$$

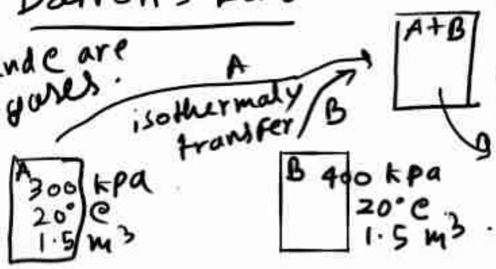
$$\therefore \frac{p_i}{P_{total}} = \frac{n_i}{n_{total}} = y_i$$

$$\Rightarrow p_i = y_i \times P_{total}.$$

$$\text{or} \quad P_{total} = \sum_{1}^{N} p_i = p_1 + p_2 + p_3 + \cdots$$

Dalton's Law

A, B, and C are ideal gases.



$$p_A = \frac{300}{700} \times 700$$

$$P_{total} = p_A + p_B = 700 \text{ kPa}.$$

$$\frac{p_A}{P_{total}} = \frac{n_i}{n_{total}} = y_i$$

$$\Rightarrow y_A = \frac{300}{700} = \frac{3}{7}$$

$$y_B = \frac{400}{700} = \frac{4}{7}.$$

$$\therefore p_A = y_A P_{total} = \frac{3}{7} \times 700 = \underline{300 \text{ kPa}}.$$

$$p_B = y_B \times P_{total} = \frac{4}{7} \times 700 = \underline{400 \text{ kPa}}.$$

Example T = 120°F, P = 13.8 psia.

	mol %
N_2	2%
CH_4	79%
C_2H_6	19%

Find the partial pressures of idividual gases.

Amagot's Law

$$V_{total} = V_A + V_B + V_C + \ldots$$

$$\therefore \frac{V_i}{V_{total}} = \frac{n_i}{n_{Total}}$$

when P and T remain same.

$$P_{N_2} = 0.2 \times 13.8 \text{ (psia.}$$

$$P_{CH_4} = 0.79 \times 13.8 \text{ (psia).}$$

$$P_{C_2H_6} = 0.19 \times 13.8 \text{ (psia).}$$

$$P_{total} = (0.2 + 0.79 + 0.19) \times 13.8$$

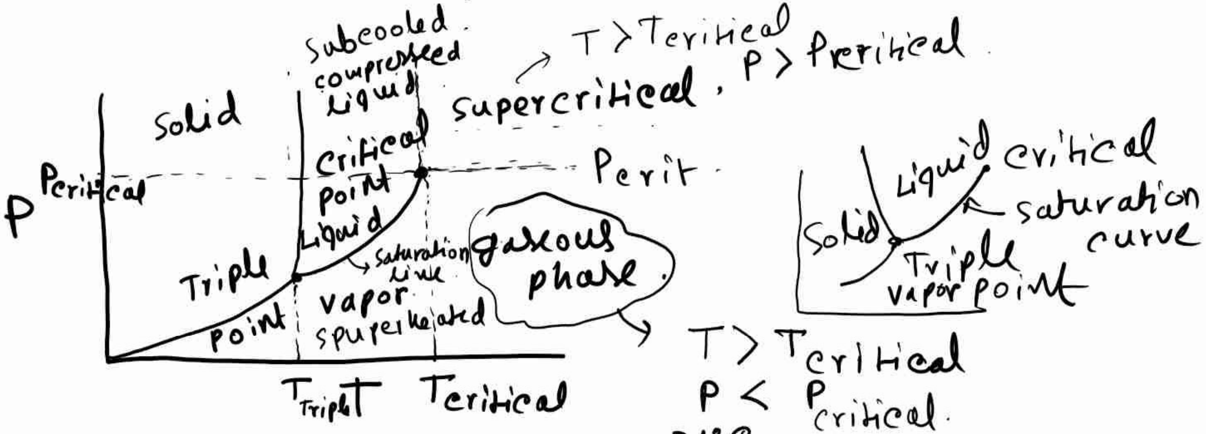
$$= \underline{\underline{13.8 \text{ psia}}}$$

Real gases.

Early experiment found that,
at the critical point all substances are in approximately the same state of molecular dispersion.

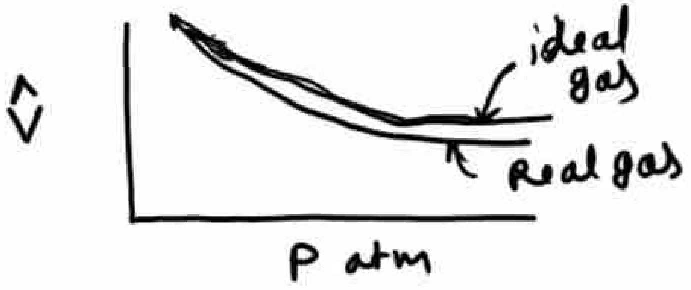
Law of corresponding State:
In the critical state all substances should behave alike. (Thermodynamic and physical properties are similar).

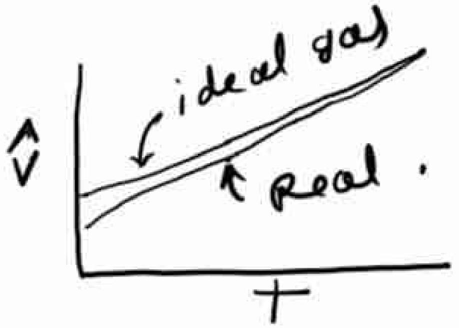
Critical state identifies the critical point. For a pure component means the maximum temperature and corresponding pressure at which liquid and vapor phases co exist.



CO_2 $T_{critical} = 31°C$.
$P_{critical} = 72.9$ atm.

CO_2 is gas above 31°C and below 72.9 atm.





Real gases coincide ideal gas.
at a lower P and higher T.

Reduced variables.

$$T_r = \frac{T}{T_c} \; ; \; P_r = \frac{P}{P_c} \; ; \; \hat{V}_r = \frac{\hat{V}}{V_c}$$

reduced T
critical T.
Reduced pressure
critical pressure
reduced volume
critical volume.

For real gases generalized equation of sate.

$$P\hat{V} = ZRT \;;\; PV = nZRT$$

$$V/n = \hat{V}.$$

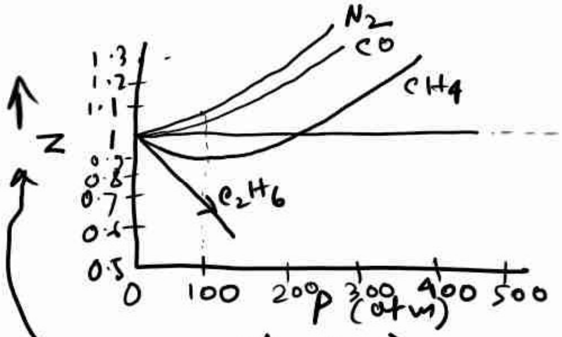
NH_3 $T = 1.0 \times T_{c\,NH_3}$

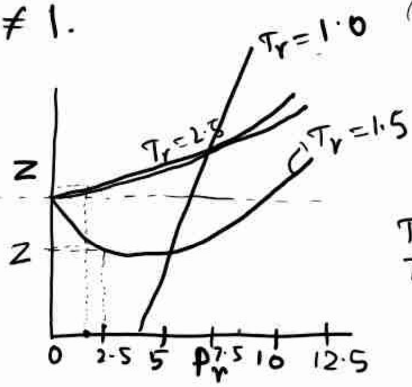
CO_2 $T = 1.0 \times T_{c\,CO_2}$.

z = compressibility factor.

for ideal gas z = 1.

but for real gas z ≠ 1.





$$Z = \frac{P\hat{V}}{RT} \longrightarrow$$

Find Z from the chart at particular P_r or P and T or T_r of the real gas. From $Z = \frac{P\hat{V}}{RT}$ relation find the property

$T = 290\,K$

$T_c = 154.4\,K$ (NH_3)

$$T_r = \frac{290}{154.4}$$

$P = 10^4$ kPa

$P_c = 50,35$ kPa.

$$\therefore P_r = \frac{10^4}{50,35}$$

find Z using the chart.

Find $\hat{V}$.

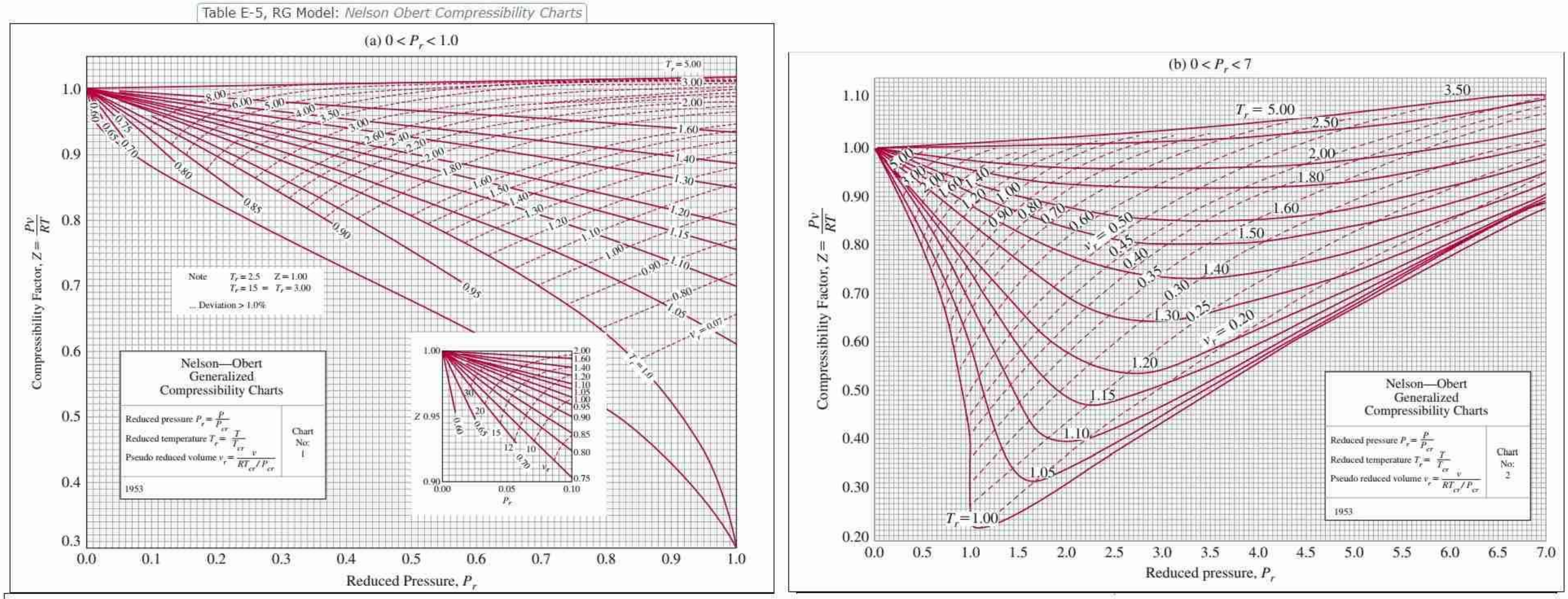
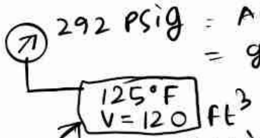


Table E-5, RG Model: *Nelson Obert Compressibility Charts*

http://eon.sdsu.edu/testhome/Test/solve/basics/tables/tablesRG/zNO.html

Referred
website



$292 \text{ psig} = \text{Absolute pressure} - \text{Atmospheric pressure}$
$= \text{gauge pressure} .$

1 atm
$= 14.7 \text{ psi}$

$$P^{\text{absolute}} = 292 + 14.7 = 306.7 \text{ psia}$$
gauge + atmospheric pressure

$$R = 10.73 \, \frac{\text{psia} \cdot \text{ft}^3}{(\text{lb-mol})(°\text{R})} .$$

$$T = 125°\text{F} + 460 = 585°\text{R} .$$

$$= 0.73 \, \frac{\text{atm} \cdot \text{ft}^3}{(\text{lb-mol})(°\text{R})} .$$

$$= 14.7 \times 0.73$$

ideal gas relationship

$$\hat{V} = \frac{RT}{P} = \frac{10.73 \times 585}{306.7} \text{ ft}^3/\text{lb-mol}$$

$$= \frac{10.73 \times 585}{306.7 \times 17_{\text{M.W}}} \text{ ft}^3/\text{lb} .$$

$$= 1.2 \ \underline{\text{ft}^3/\text{lb}} .$$

$$\text{mass of the gas} = \frac{120 \text{ ft}^3}{\hat{V}}$$

$$= \frac{120}{1.2} = \underline{\underline{100 \text{ lb}}} .$$

use

$PV = ZnRT$

$$T_c = 405.5\,K = 729.9\,°R = 405.5 \times \frac{5}{9} + 460$$

$$\hookrightarrow \frac{5}{9} + 460$$

$$P_c = 111.3 \text{ atm} = 111.3 \times 14.7 = 1636 \text{ psia}$$

$$T_r = \frac{T}{T_c} = \frac{585\,°R}{729.9\,°R} = 0.801$$

$$P_r = \frac{P}{P_c} = \frac{306.7 \text{ psia}}{1636 \text{ psia}} = 0.187;$$ from chart @ L.H.S

$$\underline{Z = 0.855}$$

$$PV_{real} = ZnRT \qquad \therefore \frac{\hat{V}_{real}}{\hat{V}_{ideal}} = \frac{Z}{1}$$

$$PV_{ideal} = nRT$$

$$\Rightarrow \hat{V}_{real} = Z \times \hat{V}_{ideal} = 0.855 \times 1.2 \text{ ft}^3/\text{lb}$$

$$= 1.03 \text{ ft}^3/\text{lb}$$

$$\text{mass of } NH_3 = \frac{120 \text{ ft}^3}{1.03 \text{ ft}^3/\text{lb}}$$

$$= \underline{\underline{117 \text{ lb}}}$$

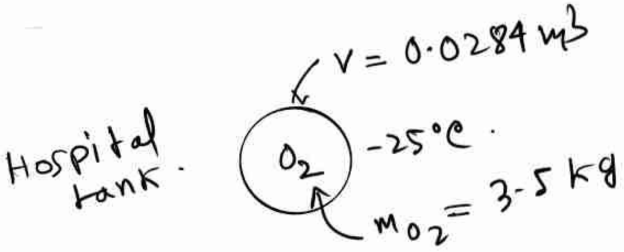
If actual data is observed

$$\hat{V} = 0.973 \text{ ft}^3/\text{lb}$$

$$m = \underline{\underline{125 \text{ lb}}}$$

error in ideal **molar volume** $= \frac{1.2 - 0.973}{0.973} \times 100\% \simeq 23\%$

error in **molar volume from Z-relation chart** $= \frac{1.03 - 0.973}{0.973} \times 100\% \simeq \underline{\underline{5.9\%}}$



Safety limit of the tank is 10^4 kPa

Is the tank safe?

$$\hat{V} = \frac{0.0284\ m^3}{\frac{3.5}{32}\ kg\ mol.}$$

$$= 0.260\ m^3/kg\ mol.$$

O_2:

$T_c = 154.4\ K$

$P_c = 49.7\ atm = 5{,}035\ kPa.$

1 atm = 101.325 kPa.

critical molar volume 1 atm = 101.325 kPa.

$$\hat{V}_c = \frac{R T_c}{P_c} = \frac{8.314 \times 154.4}{5035} \quad \frac{m^3}{kg\text{-}mol}$$

$$= 0.255\ kg\ mol.$$

$$\hat{V}_r = \frac{0.260}{0.255} = \frac{\hat{V}}{\hat{V}_c} = 1.02$$

$$T_r = \frac{248\ K}{154.4\ K} = 1.61.$$

P_r = find from chart for z vs P_r.

$= \underline{1.43}$

$P = P_c P_r$

$= 1.43 \times 5035 = 7200\ kPa.$

Safe $7200\ kPa << 10^4\ kPa.$

Pietzer acentric factor, ω.

$$z = z^0 + z'\omega \quad \text{(Appendix, C)}.$$

∴ function of P_r, T_r and ω is unique for each compound.

Table 14.1

For	ω
ammonia gas NH_3	0.25
Acetone	0.309
CO_2	0.225.
water vapor	0.344.

$P_r = 0.187$, $T_r = 0.801$. NH_3 $\omega = 0.25$

from Appendix C

$$\left.\begin{aligned} z' &= -0.103. \\ z^0 &= 0.864. \end{aligned}\right\} \text{ at } P_r = 0.187 \ \& \ T_r = 0.801.$$

$$\therefore \quad z = 0.838 \Leftarrow \boxed{z = z^0 + \omega z'}$$

use $P\hat{V} = zRT$.

Find $\hat{V}$ at a specific set of $[T, P]$ For NH_3 gas.

$$P\hat{V} = 0.838\,RT$$

Real gas mixture

Kay's method, pseudocritical values

$$P_c' = P_{cA}y_A + P_{cB}y_B + P_{cC}y_C + \cdots$$

$$T_c' = T_{cA}y_A + T_{cB}y_B + T_{cC}y_C + \cdots$$

$y_A, y_B, y_C, \cdots$ are molefractions of constituent gases in a mixture.

P_{cA} = critical pressure of, A.

T_{cA} = " T of, A

$$P_r' = \frac{P}{P_c'} \; ; \; T_r' = \frac{T}{T_c'}.$$

gas mixture	mol.	T_c (K)	P_c (atm)
CH_4	20 %	191	45.8
C_2H_4	30 %	283	50.5
N_2	50 %	126	33.5

ideal gas $T = 100°C$, $P = 90$ atm.

$$\hat{V} = \frac{RT}{P} = \frac{82.06 \times 373.15}{90}$$

$$= 340 \text{ cm}^3/\text{gmol}$$

Kay's method & compressibility chart.

$$P_c' = P_{c_{CH_4}} y_{CH_4} + P_{c_{C_2H_4}} y_{C_2H_4} + P_{c_{N_2}} y_{N_2}$$

$$= 41.1 \text{ atm.}$$

$$T_c' = T_{c_{CH_4}} y_{CH_4} + T_{c_{C_2H_4}} y_{C_2H_4} + T_{c_{N_2}} y_{N_2}$$

= 186 K

$\therefore \quad P_r' = \frac{P}{P_c'} = \frac{90}{41.1} = 2.19.$

$T_r' = \frac{T}{T_c'} = \frac{373.15}{186} = 2.01.$

$\therefore$ From Nelson, Obert chart.

at $P_r = 2.19.$ & $T_r = 2.01.$

$\underline{Z = 0.95.}$

$\hat{V} = \frac{ZRT}{P} = \frac{0.95 \times 82.06 \times 373.15}{90}$

$= 323 \text{ cm}^3/\text{gm-mol}$

$\therefore \quad \hat{V}^{\text{Nelson-obert}} - \hat{V}^{\text{ideal}} = |323 - 340|$

$\underline{\underline{= |17|}}.$

Equation of State

It is P-V-T relationship of real gases.

$\therefore$ van der Waals relation of P-V-T or van der Waals equation of state.

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

[a, b are parameters defied by van-der Walls]

$$a = \left(\frac{27}{64}\right)\frac{R^2 T_c^2}{P_c}\ \text{atm}\left(\frac{\text{cm}^3}{\text{g mol}}\right)^2$$

$\frac{a}{\hat{V}^2}$ = additional pressure

$$b = \left(\frac{1}{8}\right)\frac{RT_c}{P_c}\ \left(\frac{\text{cm}^3}{\text{g mol}}\right)$$

b = substructive molorvolume

$\therefore$ For known values of P & T

$$\therefore f(V) = V^3 - \left(nb + \frac{nRT}{P}\right)V^2 + \frac{n^2 a}{P}V - \frac{n^3 ab}{P} = 0$$

$\hookrightarrow$ V = volume.

$\therefore$ It is a nonlinear (cubic) equation.

$\therefore$ V has 3 roots. (1 root is to be taken).

take an initial guess of V.

$$\therefore V_{k+1} = V_k - \frac{f(V_k)}{f'(V_k)}$$

(Newton Raphson method).

But if V, T are known then P can be found explicitly from eqn of state, & calculated directly.

Ex:

$\swarrow$ 0.15 m^3 of cylinder

$\boxed{227\ kg}$ C_3H_8 at P_{gauge} = 4790 kPa (gauge)

Calculate temperature of the gas.

$$a = 9.24 \times 10^6 \text{ atm} \left(\frac{cm^3}{gmol}\right)^2$$

$$b = 90.7 \ cm^3/gmol.$$

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

$$\hat{V} = \frac{0.150 \times (10^{-2})^3 \ cm^3}{\dfrac{22.7 \times 10^3 \ gm}{44}} \quad (cm^3/gmol)$$

$$P^{absolute} = (4790 + \overset{1\ atm}{101.3}) \text{ kPa}.$$

$$= \frac{4790 + 101.3}{101.3} \text{ atm abs}$$

as 1 atm = 101.3 kPa.

$$= 48.3 \text{ atm absolute}.$$

$$R = 82.06 \ \frac{cm^3 \, atm}{gmol \cdot K}$$

$$\left(48.3 + \frac{a}{\hat{V}^2}\right)(\hat{V} - b) = RT$$

if $\hat{V} = \frac{V}{n}$

Put $\hat{V}$ = calculated value in ($cm^3/gmol$).

$\therefore$ T = 384 K.

Calculate $\hat{V}$ in $cm^3/gmol$ of the propane gas for this cylinder at T = 373 K.

P = 50 atm
absolute P.

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

Simplify

$$\therefore c_1\hat{V}^3 + c_2\hat{V}^2 + c_3\hat{V} + c_4 = 0$$

$$= f(\hat{V}).$$

take a initial guess of $\hat{V}$ = 90.7 $cm^3/gmol$.

$$\therefore \hat{V}^{new} = \hat{V}^{old} - \left[\frac{f(\hat{V})}{f'(\hat{V})}\right]_{\hat{V}_{old}}$$

1st iteration $\hat{V}_{old}$ = 90.7, calculate at $\hat{V}_{old}$.

$\therefore$ $\hat{V}^{new}$ = 90.7 ± constant.

2nd iteration $\hat{V}^{old}$ = $\hat{V}^{new}$ at previous/1st iteratio

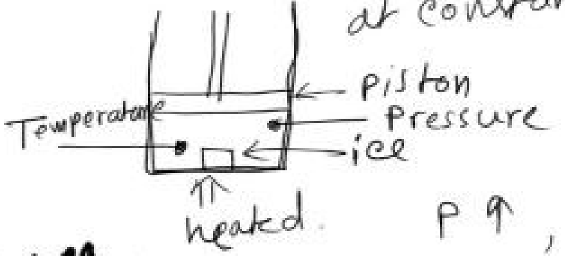
$\therefore$ say after 10 iteration

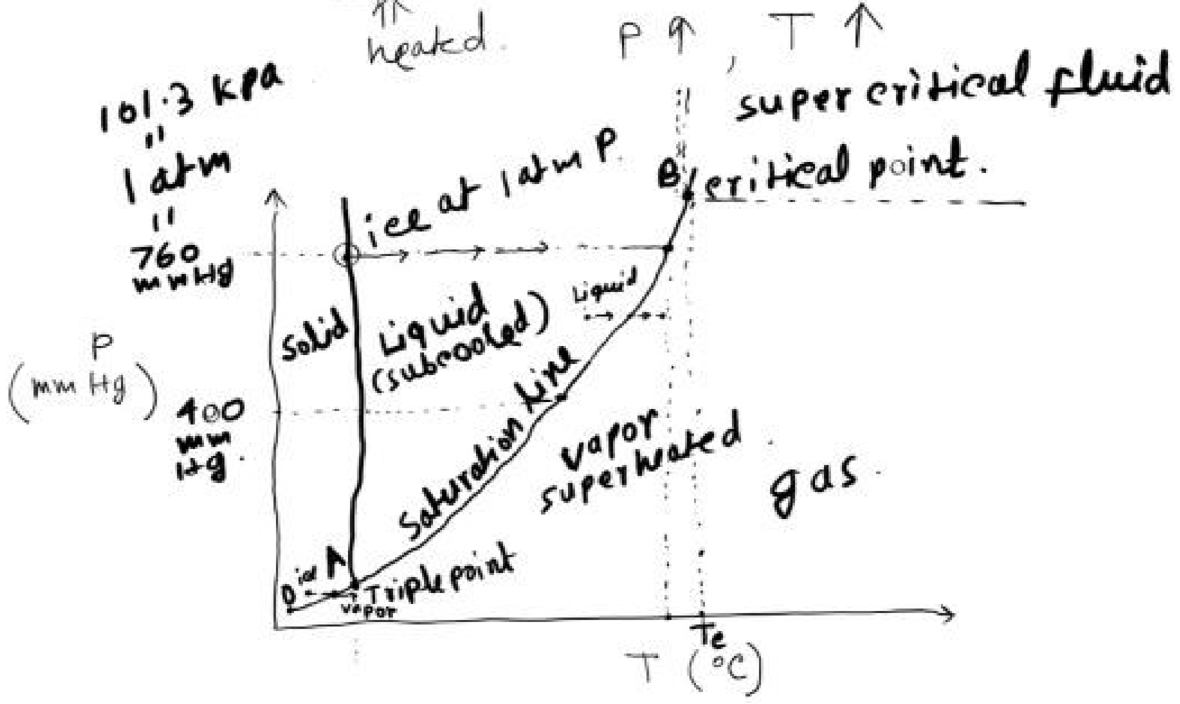
$\hat{V}^{new} - \hat{V}^{old} < 0.01$.

take $\hat{V} = \hat{V}^{new}$ after 10 iteration.

Single component 2-phase system.

at constant volume.





at saturation line liquid is saturated liquid and vapor is saturated vapor.

Saturated liquid + Latent heat of vaporization

$\Rightarrow$ saturated vapor.

Temperature of saturated liquid

= Temperature of saturated vapor at specific pressure.

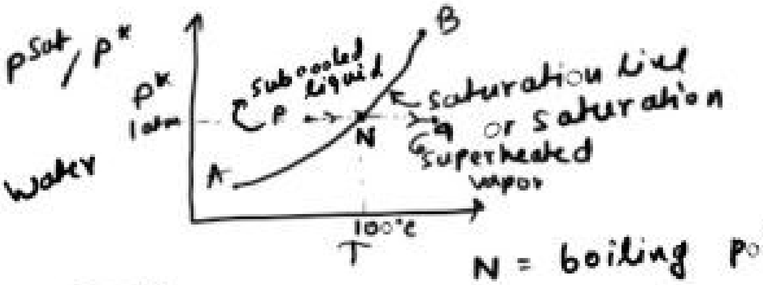
at 760 mm Hg H_2O at saturation temperature. of 100°C.

saturated water at 760 mm Hg is at 100°C.

" water vapor " " " " " 100°C

phase change occurs on the saturation line at constant temperature.

at saturation line, saturated vapor and saturated liquid will be in equilibrium at a pressure.



N = boiling point

∴ below saturation (condition) Liquid phase continues to evaporate to form vapor, untill saturation is reached.

droplet.

freesurface $= 4\pi r^2$

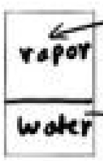
evaporation continues from the free surface (top surface here).

at saturation liquid and vapor phases come to an equilibrium.

partial pressure of vapor

= vapor pressure of the liquid at the temperature

$p^{vapor} = p^{*(liquid)}$ at same temperature.



1. atm saturation

100°C

$p^{*H_2O} = p^{H_2O}$

vapor pressure, partial pressure.

$$p^{H_2O} = P_{total}\, y_{H_2O} = p^{*H_2O} =$$

$$p_{total} = p^{H_2O} + p^{air\,dry}.$$

Antonie equation

$$\ln p^* = A - \frac{B}{C+T} \quad (T \text{ is in K})$$

$$\ln p^{sat} = A - \frac{B}{C+T} \quad (p^* \text{ is in mm Hg}).$$

A, B, and C are constants.

For water Appendix G

$A = 18.3036$, $B = 3816.44$

$C = -46.13$.

Clapeyron equation

$$\frac{dp^*}{dT} = \frac{\Delta \hat{H}_v}{T(\hat{V}_g - \hat{V}_l)}$$

$\Delta \hat{H}_v$ = Latent heat of vaporization, J/kg mol

$\hat{V}_g$ = specific volume of gas, m³/kg mol

$\hat{V}_l$ = " " " liquid, m³/kg mol

Clapeyron

assumed ideal gas law

$$\hat{V}_g = RT/p^*$$

$$\therefore \quad \hat{V}_l << \hat{V}_g \quad (\text{neglect } \hat{V}_l).$$

$$d\ln p^* = \frac{dp^*}{p} = \frac{\Delta \hat{H}_v \, dT}{RT^2} =$$

$$\log_{10}\frac{p_1^*}{p_2^*} = \frac{\Delta \hat{H}_v}{2.303R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Clausius-Clapeyron equation

∴ Find p_1^* and p_2^* using Antonie equation, and find $\Delta \hat{H}_v$.

Gibbs phase rule

$$F = C - P + 2$$

F = number of degree of freedom

(number of independent properties that have to be specified to determine all intensive properties of each phase of the system).

ρ, $\hat{V}$, T, P intensive properties. independent of mass.

P = number of phase

C = " " component (species).

* For ideal gas of pure form. (say, N_2 or O_2)

$C = 1$; $P = 1$;

$\therefore F = 1 - 1 + 2 = 2$.

$PV = nRT$ (need to specify 2 intensive properties).

say, T and P are specified

$\hat{V}$ can be calculated. (system is fixed).

* at triple point $P = 3$. (vapor, solid, liquid)

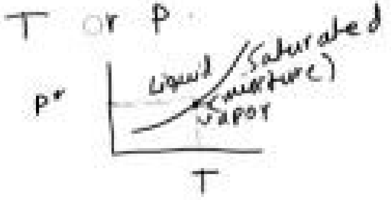
$C = 1$.

$\therefore F = 1 - 3 + 2 = 0$

* pure component vapor & liquid mixture say water vapor + water liquid.

$\therefore C = 1$, $P = 2$ $\therefore F = 1 - 2 + 2 = 1$.

$\therefore$ specify T or P.

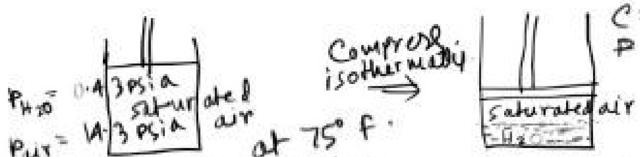


* 2 compone 2

air, water system

$\therefore F = 2 - 2 + 2 = 2$

$\therefore$ need to specify: T, P
or P, mole fraction
or T, mole fraction.



$P_{H_2O} = 0.43$ psia

$P_{air} = 14.3$ psia

at 75° F.

$P_T = 14.3 + 0.43$
$= 14.7$ psia. 1 atm

$C = 2$ (air, H_2O)
$P = 2$ (air, H_2O).

$P_{H_2O} = 0.43$ psia.
$P_{air} = 58.4$ "
$P_{Total} = 58.83$ psia.
at 75°F and 4 atm.

Specify. T, P. and P_{H_2O} or mole fraction is known.

T, mole fraction and P is known
→ mole fraction of H_2O in air.

Here, $\dfrac{n_{H_2O}}{n_{air}} = \dfrac{P_{H_2O}}{P_{air}}$. Humidity chart.

$\therefore \dfrac{x_{H_2O}}{x_{air}} = \dfrac{P_{H_2O}}{P_{air}}$. psychrometric chart.

* Benzene and toluene.
(vapor & liquid mixture).

$\therefore C = 2.,\ P = 2.$

$F = C - P + 2 = \textcircled{2}$ T, P then mole fraction will be known.

Ideal solution

all of the molecule should have same size

all " " " " " " molecular interaction.

ex. Benzene & toluene, or xylene.

Hexane & cyclohexane

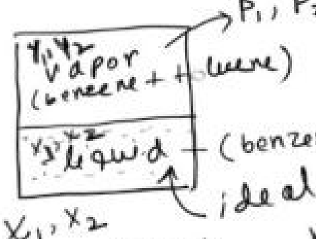
∴ Raoult's law (valid for ideal solution)

$$p_i = x_i \, p_i^*(T).$$

p_i = partial pressure of component i in vapor phase

x_i = molefraction of component i in liquid phase.

p_i^* = vapor pressure of component i at Temperature T



$$P_T = \underbrace{P_1}_{\text{benzene partial pressure}} + P_2 \rightarrow \text{toluene partial pressure}$$

$$\left.\begin{aligned} x_1 + x_2 &= 1 \\ y_1 + y_2 &= 1. \end{aligned}\right\}$$

1 = benzene,
2 = toluene.

x_1 = mole fraction of benzene in liquid phase

x_2 = mole fraction of toluene in liquid phase.

∴ Roult's law.

$p_1 = x_1 p_1^*(T)$.
↳ pure state vapor pressure

if x_1 and T are known.
Find $p_1^*(T)$ from Antonie eqn.

and Find p_1 from Roult's law

∴ Take vapor phase is ideal gas.

∴ $p_1 + p_2 = p_T$ (Dalton's law).

$y_1 p_T + y_2 p_T = p_T$

$$\left\{ \begin{aligned} p_1 &= y_1 p_T \\ p_2 &= y_2 p_T \end{aligned} \right.$$

y_1 & y_2 are mole fraction of benzene and toluene in vapor phase.

∴ y_1, y_2 are known

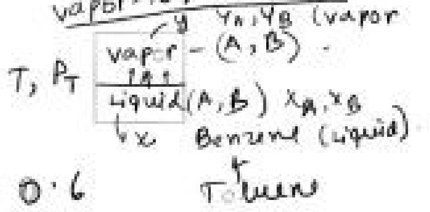
∴ Roult's law and ideal gas law can be combined.

$$\left. \begin{aligned} \therefore p_1 = y_1 p_T &= x_1 p_1^*(T) \\ p_2 = y_2 p_T &= x_2 p_2^*(T) \end{aligned} \right\}$$

Roult's law

$y_i p_T = x_i p_i^*(T) = p_i$

vapor-liquid equilibrium



you specify. x and T.

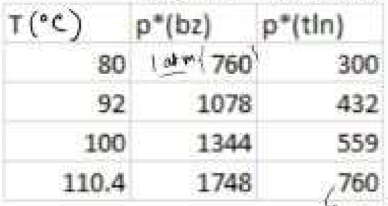
Liquid $\begin{cases} \text{benzene} & 0.4 \\ \text{Toluene} & 1 - 0.4 = 0.6 \end{cases}$

∴ p_1, p_2 can be found from Roult's law. and y_1, y_2 can be found from ideal gas law.

as $p_1 + p_2 = p_T$ (will be known) and all intensive properties such as y, p_T will be known).

Vaporpressure (mm Hg) [From Antonie's equation]

Temperature Benzene Toluene



T(°C)	p*(bz)	p*(tln)
80	1 atm{760}	300
92	1078	432
100	1344	559
110.4	1748	760 1 atm

← At 1 atm pressure

$P_T = 1$ atm , 2 atm

90°C - 120°C

80°C - Boiling point of pure Benzene at 1 atm.

110.4°C Boiling point of pure toluene at 1 atm.

at boiling point vapor pressure must be greater than equal to absolute pressure (1 atm).

Plot T-x-y using Rault's law

$$p_{Bz} = x_{Bz} p^*_{Bz}(T) = P_T y_{Bz} \rightarrow \text{Benzene}$$

$$p_{tl} = x_{tln} p^*_{tln}(T) = P_T y_{tln} \rightarrow \text{toluene}$$

$y_{Bz} + y_{tln} = 1$; $x_{Bz} + x_{tln} = 1$;

Add 2 equation ①

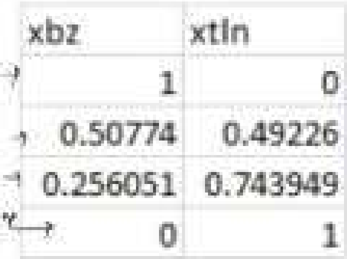
$$P_T (y_{Bz} + y_{tln}) = x_{Bz} p^*_{Bz}(T) + x_{tln} p^*_{tln}(T)$$

$$P_T = x_{Bz} P^*_{Bz} + (1 - x_{Bz}) P^*_{tln}$$

$$\therefore P_T - P^*_{tln} = x_{Bz} (P^*_{Bz} - P^*_{tln})$$

$$\Rightarrow x_{Bz} = \frac{P_T - P^*_{tln}(T)}{P^*_{Bz}(T) - P^*_{tln}(T)}$$

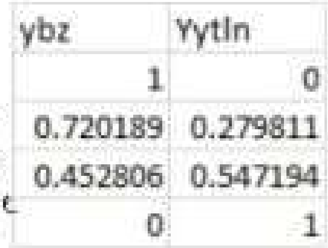
$$\therefore x_{tln} = (1 - x_{Bz})$$



	xbz	xtln
80°C →	1	0
92°C →	0.50774	0.49226
100°C →	0.256051	0.743949
110.4°C →	0	1

$$\frac{760-300}{760-300}=1$$

$$\frac{760-432}{1078-432}=0.5077$$



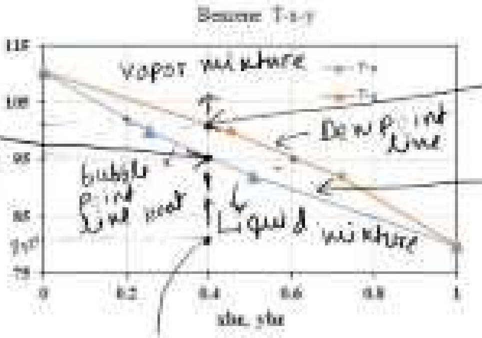
	ybz	Yytln
80°C	1	0
92°C	0.720189	0.279811
100°C	0.452806	0.547194
110.4°C	0	1

$$y_{BZ}=\frac{P^*_{BZ}(T)\cdot x_{BZ}}{P_T}$$

$$\frac{760\times 1}{760}=1.$$

$$y_{BZ}=\frac{1078\times 0.5}{760}=\underline{\underline{0.7201}}$$

$$\underline{y_{tln}=1-y_{BZ}}$$



bubble point

dew point temperature.

2 phase region. vapor-liquid mixture.

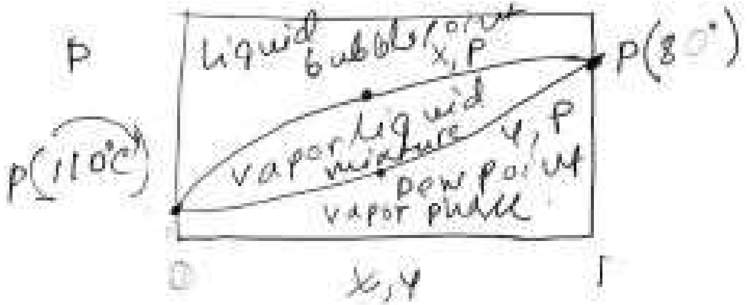
40% benzene and 60% toluene in a liquid mixture

At bubble point boiling Starts from a liquid mixture

At dew point boiling stops. From the vapor liquid mixture.

/first drop of vapor will be condensed from a vapor mixture.

higher boiling point lower is vapor pressure constant T



90°C calculate vapor pressure of Benzene
from Antonie
equ.

$$\ln p_i^* = A - \frac{B}{C+T} \rightarrow \underline{\underline{T = 90°C}}$$

$p^*_{Bz} =$ mmHg

$p^*_{Tln} =$ mmHg $T = 90°C$

cal

P x Y. :.

Bz — Tln
1070 mmHg — 430 mmHg

P 430
500
600
700
1000
1070

$$P_T = x_{Bz} \overline{p^*_{Bz}} + (1 - x_{Bz}) \overline{p^*_{Tln}}$$

x_{Bz}

430
500
7..

At 90°C construct P_T - x - y curve for
Benzene - toluene mixture.

plot P - x - y for Benzene only.

take A, B, C data from
<u>book</u>

Henry law

valid for

$p_i = H_i x_i$ [dilute gas dissolved in liquid at equilibrium]

p_i = partial pressure in gas phase of the dilute constituent.

x_i = its mole fraction in. H_i = Henry law constant.

here $x_i \to 0$, $p_i \to 0$.

at 40°C CO_2 H_{CO_2} = 69,600 atm/molefraction

$\underline{x_{CO_2} = 4.2 \times 10^{-6}}$.

44000 ppm.

$$\frac{44{,}000 \text{ gm } CO_2}{10^6 \text{ gm air}}$$

$$\Rightarrow \frac{44000/44\,(CO_2)}{10^6/29\,(\text{air})}$$

$$p_{CO_2} = 4.2 \times 10^{-6} \times 69000$$

$$= \underline{0.29 \text{ atm}}$$

p_T = 1 atm.

Psychrometrics

Gas + vapor   mixture

air + water vapor   "

↓ N_2, O_2, CO_2 fixed. compoisition

↓ moisture H_2O molecule composition will change.

At differnt temperature pressure moisture content (mole ratio of H_2O) in air will vary.

Air is saturated by water vapor.

means

partiatial pressure of H_2O in air = vapor pressure of H_2O at the same temperature.

Ideal gas Dalton Law   same temperature.

P_T = total pressure of (air + H_2O) air.

$$P_T = P_{air} + P_{H_2O}$$

100 kPa = 97 kPa + 3 kPa. (at same T).

mole fraction of H_2O $y_{H_2O} = \frac{3}{100}$.

" " dry air $y_{air} = \frac{97}{100}$

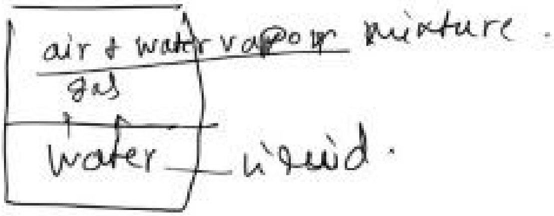
mole fraction of H_2O $y = \frac{\text{mole of } H_2O}{\text{Total mole of air}}$

mole ratio $Y = \frac{\text{mol of } H_2O}{\text{mol of dry air}}$.

$$\boxed{Y = \frac{y}{1-y}}$$

Say mol fraction of H_2O in air = 0.03 $\frac{\text{mol } H_2O}{\text{mol of air}}$.

$$\underline{\underline{Y = \frac{0.03}{1-0.03} \; \frac{\text{mol } H_2O}{\text{mol of dry air}}}}$$



∴ Rault's law

$$p_{H_2O} = x_{H_2O} \, p^*_{H_2O}.$$

pure water.

$x_{H_2O} = 1$.

∴ $p_{H_2O} = p^*_{H_2O}$ at <u>saturation</u>.

20°C saturated air water mixture.

∴ $p_{H_2O}^{\text{air mixture}}$ = vapor pressure of water at 20°C.

Specific heat of dry air

at 1 atm (101·325 kPa), specific heat of dry air C_{pa} (−40 − 60°C) - varying from 0·997 — 1·022 kJ/(kg.K) or $kJ.kg^{-1}.K^{-1}$.

Average value of 1·005 $kJ.kg^{-1}.K^{-1}$ is used.

Enthalpy of dry air

Enthalpy of dry air, $H_a = 1{\cdot}005\,(T_a - T_0)$.

$$= C_{pa}(T_a - T_0)\ kJ.kg^{-1}$$

T_a = dry bulb temperature.
T_0 = reference temperature, 0°C.

Dry bulb temperature T_{db}

It refers basically to the ambient air temperature. It is indicated by a thermometer not effected by the moisture of the air. The termometer is freely exposed to air but shielded from radiation and moisture.

Wet bulb temperature : T_{wb}

It is measured by using a thermometer with the bulb covered with a wet wick.
It is the adiabatic saturation temperature.

$$\therefore\quad T_{db} - T_{wb} = f(\text{humidity}) \geq 0$$

Dew point temperature T_{dp}.

It is the temperature where vapor starts to condense out of the air (the temperature at which air becomes completely saturated).

Humidity ratio W

It is defined as the mass of water vapor per unit mass of dry air.

$$W = \frac{m_w}{m_a} \quad \text{kg water / kg dry air}$$

$$W = \frac{18.015}{28.9645} \frac{x_w}{x_a} = 0.622 \frac{x_w}{x_a}.$$

x_w = mole fraction of water vapor.
x_a = mol fraction of dry air.

Now $p_a V = n_a R T$ — (i)
$p_w V = n_w R T$ — (ii)

Summing gives. $(p_a + p_w) V = (n_a + n_w) R T$ — (iii)

Now dividing by earlier equations. $(i \div iii)$ & $(ii \div iii)$.

$$\frac{p_a}{p_a + p_w} = \frac{n_a}{n_a + n_w} = x_a$$

$$\frac{p_w}{p_a + p_w} = \frac{n_w}{n_a + n_w} = x_w$$

$$\therefore \quad W = 0.622 \frac{p_w}{p_a}. \quad \left[\text{as } \frac{p_w}{p_a} = \frac{x_w}{x_a}\right]$$

Since $p_a = p_B - p_w$

$$\therefore W = 0.622 \frac{p_w}{p_B - p_w} \quad \text{kg water / kg dry air}$$

Relative Humidity ϕ.

it is the ratio of molefraction of water vapor in a given moist air sample to the molefraction in an air sample saturated at the same. pressure.

$$\phi = \frac{x_w}{x_{ws}} \times 100 .$$

$$\text{or } \phi = \frac{P_w}{P_{ws}} \times 100\% .$$

P_{ws} = saturation pressure of water vapor.

x_{ws} = molefraction of saturated water.

For perfect gas law.

$$\phi = \frac{\rho_w}{\rho_s} \times 100\% .$$

ρ_w = density of water vapor in air (kg/m³)

ρ_s = density of saturated water vapor. at the T_{db}, kg/m³

- It does not measure absolute amount of moisture in the air.
- It provides a a measure of the amount of moisture in the air relative to the maximum amount of moisture in air saturated at T_{db}.
- As $T_a \uparrow$ the maximum moisture content of the air $\uparrow$.

$$\therefore \phi \simeq f(T_a) .$$

Partial pressures and temperatures of air-vapor mixtures, developed by Carrier is given by,

$$P_W = P_{Wb}^{S} - \frac{(P_B - P_{Wb}^{S})(T_a - T_{Wb})}{1555.56 - 0.722 T_{Wb}}$$

P_W = partial pressure of water vapor at dew point temperature (kPa).

P_B = Barometric pressure (kPa).

P_{Wb}^{S} = saturation pressure of water vapor at the wet bulb temperature (kPa)

T_a = dry bulb temperature, °C

T_{Wb} = wet bulb temperature, °C.

Problem

Find dew point temperature, humidity ratio, humid volume, and relative humidity of air having a dry bulb temperature of 40°C and wet bulb temperature of 30°C.

Table A.4.2 { vapor pressure at 40°C = 7.384 kPa.
" " at 30°C = 4.246 kPa.

$$P_W = 4.246 - \frac{(101.325 - 4.246)(40-30)}{1555.56 - 0.722 \times 30}$$

$$= 3.613 \text{ kPa}.$$

From A-4-2 corresponding temperature
For 3.613 kPa vapor pressure is 27.2°C.

$\therefore$ $T_{dp} = 27.2°C$ (dew point).

Humidity ratio $W = 0.622 \times \frac{3.613}{101.325 - 3.613}$

$\left(0.622 \times \frac{P_W}{P_B - P_W}\right)$.

$= 0.023$ kg water/kg dry air.

Humid volume.

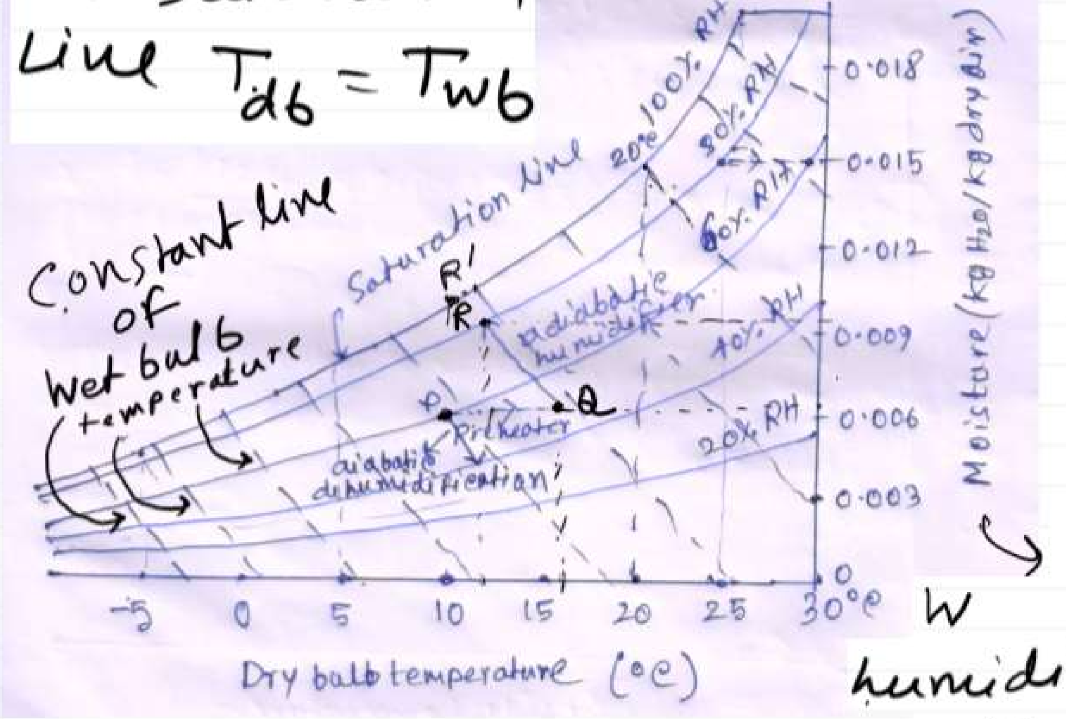
$V_m' = (0.082 \times 40 + 22.4)\left(\frac{1}{29} + \frac{0.023}{18}\right)$

$= 0.918$ m³/kg dry air.

<u>Relative humidity</u>

$\phi = \frac{3.613}{7.384} \times 100 = 48.9\%$.

at 100% R.H
or saturation
Line $T_{db} = T_{wb}$



W
humidity
ratio

Psychometry chart.

- Transport Processes and Unit Operations, (3^{rd} ed), C.J. Geankoplis, 1993, Prentice-Hall International, Inc.

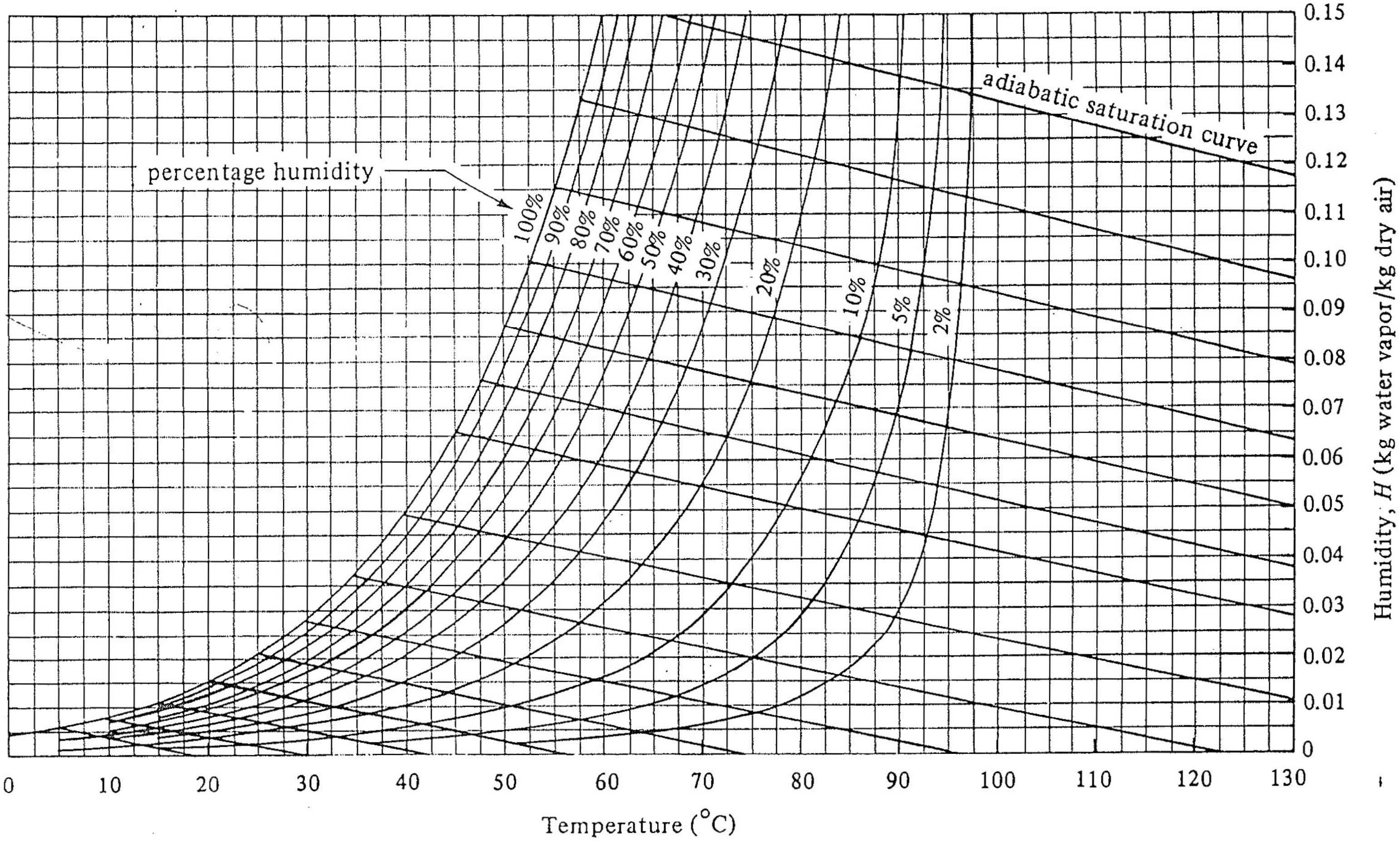


FIGURE 9.3-2. *Humidity chart for mixtures of air and water vapor at a total pressure of 101.325 kPa (760 mm Hg). (From R. E. Treybal, Mass-Transfer Operations, 3rd ed. New York: McGraw-Hill Book Company, 1980. With permission.)*

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