Department of Chemical Engineering Thapar Institute of Engineering & Technology, Patiala

Course: Material and Energy Balances UCH301

Course Instructor:

Dr. R. K. Gupta, Professor, Chemical Engineering

Gas Laws, Roult's Law, Henry's Law

Ideal Gas Law (Equation of State)

- An equation of state relates the molar quantity and volume of gas (or specific volume of a gas) with temperature and pressure.

- Ideal Gas Law (equation of state):
$$PV = nRT$$

✔ A gas whose PVT behavior obeys this equation is said to be an ideal gas or perfect gas

✔ *The above ideal gas equation finds a very wide use in chemical engineering practice as you will learn from various courses in senior years.*

✔ The standard conditions most commonly used are Standard temperature ($0\ ^{0}C$ or 273 K) and standard pressure (1 atm).

- Dalton's Law: Sum of partial pressures of all components in an *ideal gas mixture* is equal to total pressure:

$$P = p_1 + p_2 + p_3$$

(where P is total pressure of the mixture, and p_1, p_2, p_3 are the partial pressures of component 1, 2 and 3 present in the mixture)

- Amagat's Law: Sum of partial volumes of all components in an ideal gas mixture is equal to total Volume:

$$V = v_1 + v_2 + v_3 + \text{-------}$$

(where V is total Volume of the mixture, and v_1, v_2, v_3 are the partial volumes of component 1, 2 and 3 present in the mixture)

Exercise

Butane (C_4H_{10}) at 36^0 C and 3 atm absolute flows into a reactor at a rate of 1100 kg/h. Calculate: the volumetric flow rate of this stream using conversion from standard conditions.

SOLUTION

one kmol/h of gas has 22.4 m^3/h volumetric flow rate at 273 K and 1 atm.

Molecular weight of C_4H_{10}= 58 kg/kmol

Thus volumetric flow rate is = 22.4*110/58

$\qquad\qquad\qquad\qquad$ = 42.48 m^3/h

At standard conditions: $$P_1V_1 = n_1RT_1$$

At given conditions: $$P_2V_2 = n_2RT_2$$

Since $n_1 = n_2$

Dividing $V_2 = V_1 * \{P_1T_2\}/\{P_2T_1\}$

$= 42.48 * \{1*309\}/\{3*273)$

$= 16 \text{ m}^3/\text{h}$

Roult's Law & Henry's Law

- *Before we discuss these laws we need to understand few terms which are relevant to these.*

- Any substance has an infinite number of boiling points, *normal boiling point is the temperature at which boiling takes place under a pressure of 1 atm*.

- When a liquid is heated slowly at constant pressure, the temperature at which first vapor bubble is formed is the bubble point temperature of the liquid at the given pressure.

- When a vapor is cooled slowly at constant pressure, the temperature at which the first drop of liquid is formed is known as dew point temperature.

  (Cooling causes vapor to become saturated at the dew point)

Vapor Pressure

Vapor or liquid phases alone, may exist over a wide range of conditions.

At a given temperature there is only one pressure at which the liquid and vapor phases of a pure substance may exist in equilibrium.

Vaporization and condensation are equilibrium processes, and the equilibrium pressure is called the vapor pressure.

<u>A saturated gas contains all the liquid that it can hold at the system temperature and pressure.</u>

<u>ROULT'S LAW</u>

   If a gas at temperature ,T, and pressure , P, contains a saturated vapor whose mol fraction is y_A, then the partial pressure of the vapor in the gas phase equals the product of pure-component vapor pressure p_A^* and its mol fraction in the liquid phase (at the system temperature)

$$\mathbf{p_A = x_A p_A^*(T)} \qquad \text{(Also, } p_A = P^*y_A\text{)}$$

   Where $p_A^*(T)$ is the pure component vapor pressure of component A at temperature T.

   (This law relates liquid phase composition with vapor phase composition at equilibrium)

Henry's law:

It states that the partial pressure of a component in gas phase is proportional to its mol fraction in liquid phase:

$$p_A = y_A P = x_A H_A$$

Proportionality factor is Henry's constant.

(Values of Henry's constant for several components are available in literature)

✔ Both Roult's law and Henry's law provide relationships between partial pressure of A in gas phase, p_A, and mol fraction of A in liquid phase, x_A. Henry's law gives good approximation for dilute solutions.

REAL GASES

Equation of State for Real Gases

- The ideal gas equation is simplest and most convenient equation of state. This can be easily solved and the calculations are independent of the species of the gas. Its shortcoming is that it can be considerably inaccurate for non ideal/real gases.

- At high pressures or at very low temperatures the specific volume predicted by the ideal gas equations may be 2 or three times in either direction than the actual value.

Real Gases

Compressibility factor equation of state:

$$z = \frac{P\hat{V}}{RT} \qquad \hat{V} = V/n$$

or

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

$$PV = znRT$$

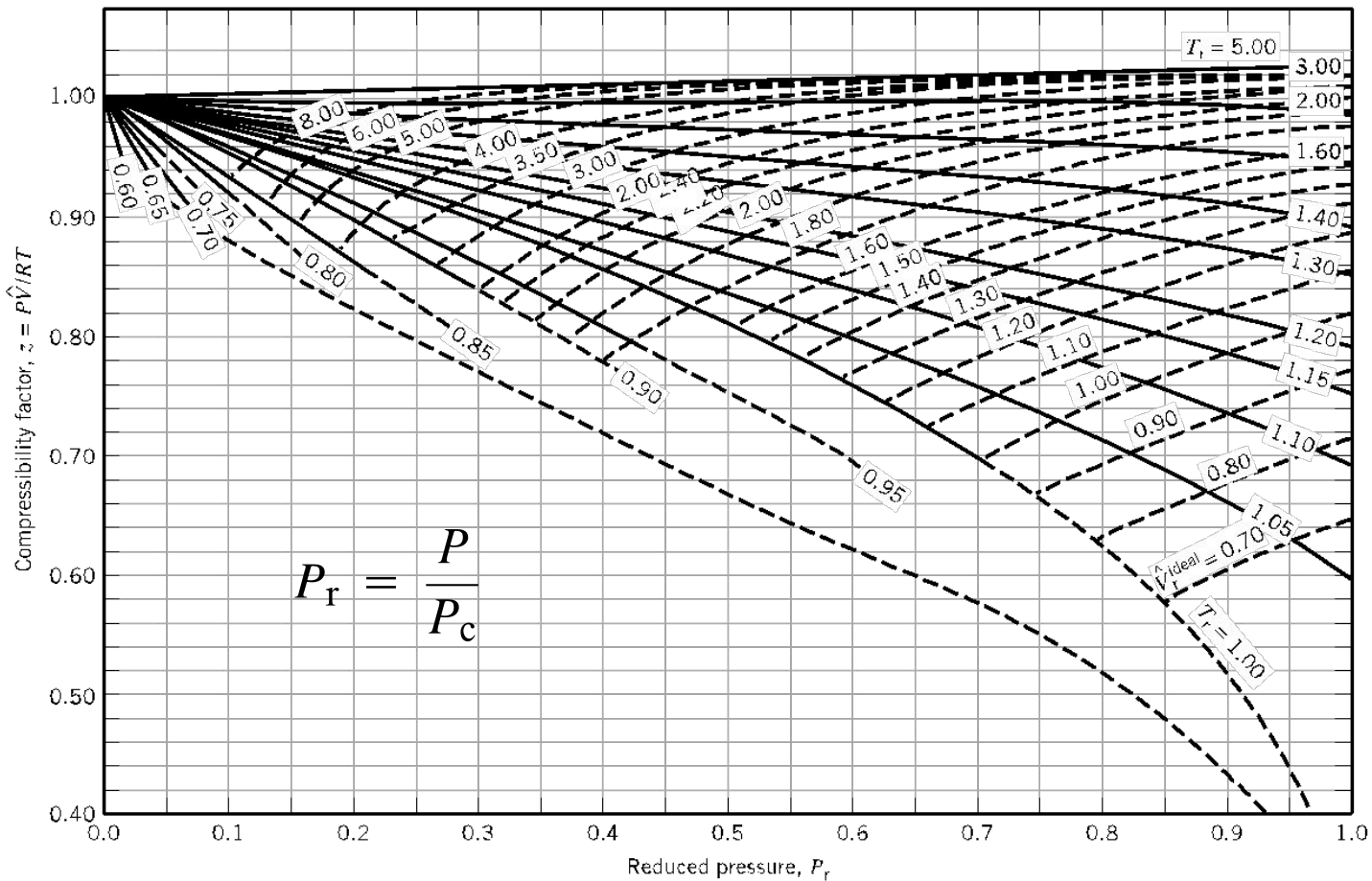z is a measure of the deviation of the gas from ideal behavior

If z = 1 → ideal gas

The values of z are available in literature as a function of T and P

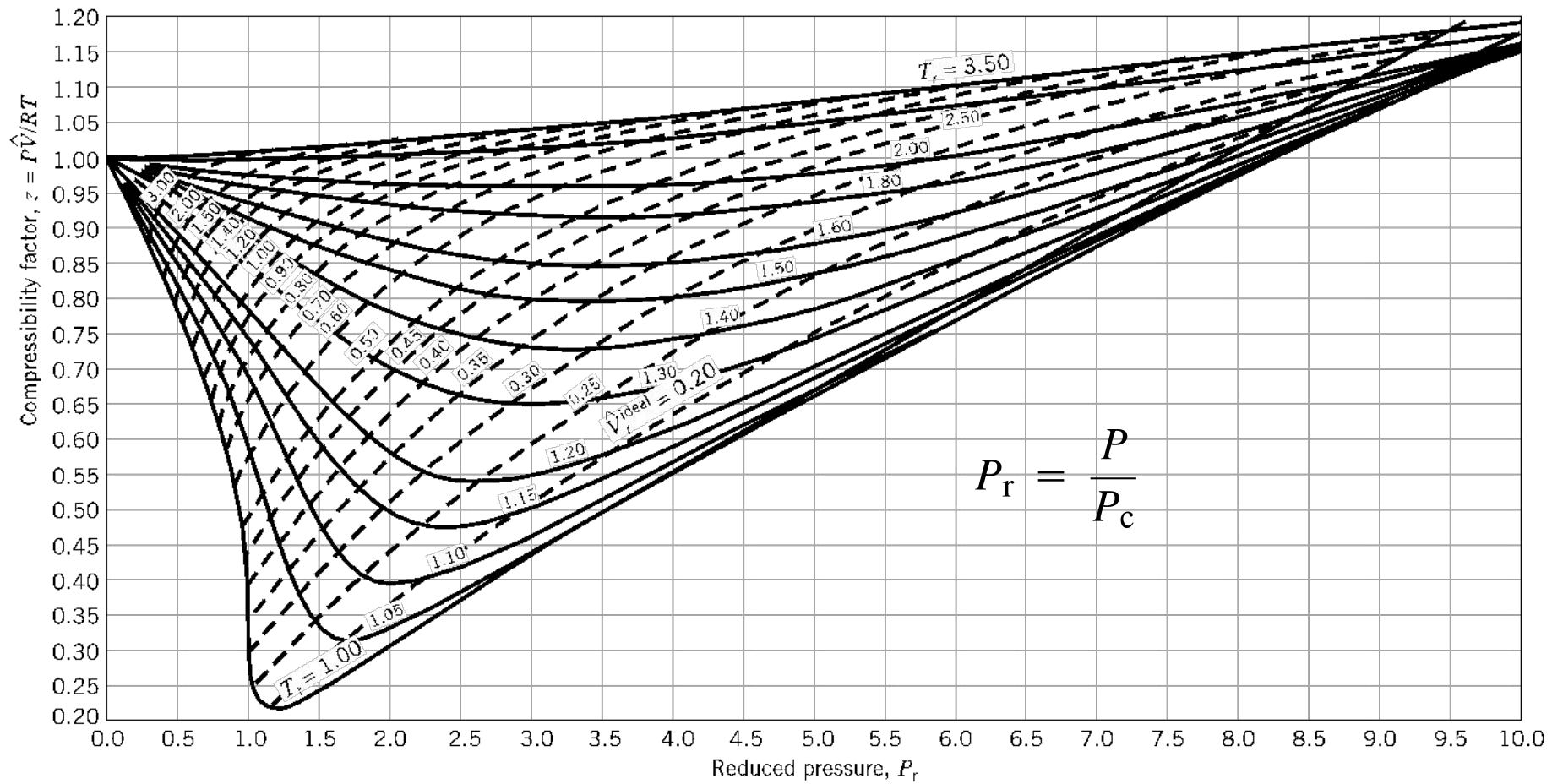- The following chart gives the comilation of values of z as a function of reduced Pressure (P_r),

Compressibility chart, medium pressure (Ref. D.M. Himmelblau)

$$P_r = \frac{P}{P_c}$$

Compressibility chart, high pressure (Ref. D.M. Himmelblau)