# ESO201A : THERMODYNAMICS
# 2021-22 Ist semester
# IIT Kanpur

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## Lecture 6

# Gaseous state :

A pure substance is said to be in a gaseous state if it does not condense upon cooling or compression in a given process.

Thus if the temperature and pressure of a pure substance is above the values corresponding to critical point, then it is generally considered as a "gas".

Recall that according to the **state postulate** (based on experimental observations) , the state of a single phase of a pure substance is completely determined by specifying two independent, intensive variables.

The state postulate certainly applies to a gas.

# Equation of state :

Thus state postulate implies that if we consider any intensive property $\theta$, then $\theta = f(T,P)$ or $\theta = g(T,v)$. This is because $(T,P)$ and $(T,v)$ are sets of two independent intensive variables. The property $\theta$ can be specific heat, specific volume, viscosity etc.

If we use $\theta = v$ (specific volume), then $v = f(T,P)$. This equation is known as "Equation of state". Note that $v$, $T$, $P$ are all experimentally measurable properties. Hence equation of state can be obtained from experimental measurements.

If we make certain approximations, we can obtain equation of state theoretically (using statistical mechanics). One such approximation is to assume that a given gas phase is an "Ideal gas" , i.e., the constituent molecules/atoms of the gas do not interact with each other.

# Ideal gas equation of state :

For an ideal gas, it can be shown that

$$v = \frac{RT}{P} \; , \; \text{where} \; R = \frac{R_u}{M}$$

$R_u$ = 8.314  kJ/(kmol.K) is universal gas constant,  and

M = molecular weight in (kg/kmol) or (g/mol)

For example, for $N_2$,  M = 28 kg/kmol  and hence R = 0.297 kJ/(kg.K)

Table A-1 (of textbook) lists M, R ,and critical points for several gases.

It is partially reproduced below :

Ref.  Cengel and Boles , 8th Edition (2015)

## TABLE A–1

Molar mass, gas constant, and critical−point properties

| Substance | Formula | Molar mass, $M$ kg/kmol | Gas constant, $R$ kJ/kg·K* | Critical-point properties Temperature, K | Pressure, MPa | Volume, $m^3$/kmol |
|---|---|---|---|---|---|---|
| Air | — | 28.97 | 0.2870 | 132.5 | 3.77 | 0.0883 |
| Ammonia | $NH_3$ | 17.03 | 0.4882 | 405.5 | 11.28 | 0.0724 |
| Argon | Ar | 39.948 | 0.2081 | 151 | 4.86 | 0.0749 |
| Benzene | $C_6H_6$ | 78.115 | 0.1064 | 562 | 4.92 | 0.2603 |
| Bromine | $Br_2$ | 159.808 | 0.0520 | 584 | 10.34 | 0.1355 |
| $n-$Butane | $C_4H_{10}$ | 58.124 | 0.1430 | 425.2 | 3.80 | 0.2547 |
| Carbon dioxide | $CO_2$ | 44.01 | 0.1889 | 304.2 | 7.39 | 0.0943 |
| Carbon monoxide | CO | 28.011 | 0.2968 | 133 | 3.50 | 0.0930 |
| Carbon tetrachloride | $CCl_4$ | 153.82 | 0.05405 | 556.4 | 4.56 | 0.2759 |
| Chlorine | $Cl_2$ | 70.906 | 0.1173 | 417 | 7.71 | 0.1242 |
| Chloroform | $CHCl_3$ | 119.38 | 0.06964 | 536.6 | 5.47 | 0.2403 |
| Dichlorodifluoromethane (R−12) | $CCl_2F_2$ | 120.91 | 0.06876 | 384.7 | 4.01 | 0.2179 |
| Dichlorofluoromethane (R−21) | $CHCl_2F$ | 102.92 | 0.08078 | 451.7 | 5.17 | 0.1973 |
| Ethane | $C_2H_6$ | 30.070 | 0.2765 | 305.5 | 4.48 | 0.1480 |

# When can a gas be approximated as an ideal gas ?

In general, when the constituent molecules/atoms are far apart from each other, there is not a significant intermolecular interaction

This condition is approached as we increase the temperature or decrease the pressure of the gas.  Generally under ambient conditions (P = 1 atm and T = 25 $^0$C), many gases can be considered as ideal gases to a good degree of approximation.

Can water vapor be considered as Ideal gas ?

Generally if the pressure of water vapor is less than 10 kPa, then yes !  It can be considered as ideal gas without introducing serious error in calculations.  (see next slide for details)

Ref. Cengel and Boles , 8th Edition (2015)
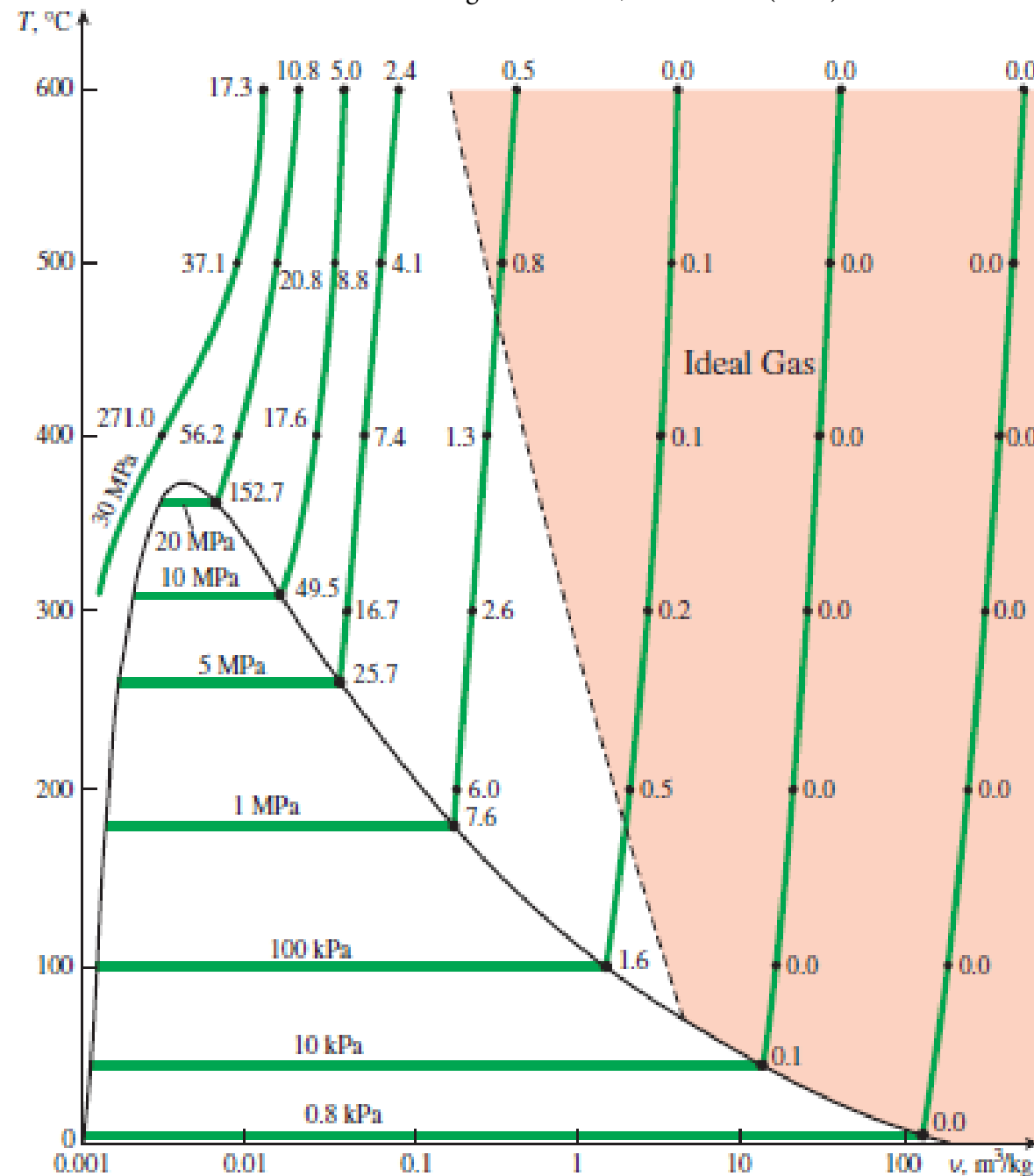
The numbers without the units are the percentage errors calculated as below:

$$Error(\%) = \left[ \frac{v(actual) - v(ideal)}{v(actual)} \right] \times 100$$

Here v(ideal) is the specific volume obtained from ideal gas equation of state and v(actual) is the actual value of the specific volume as listed in steam tables.

Below 10 kPa, error is less than 0.1%

In the shaded region, error is less than 1%

Near the critical point and near the saturation vapor states with P > 100kPa, error is large

## Compressibility factor (Z):

It measures the deviation of the actual gas from ideal-gas behavior. It is defined as follows:

$$Z = \frac{Pv}{RT}$$

Note that for an ideal gas, Z = 1.    It has been experimentally observed that :

*The values of Z at a given reduced temperature ($T_R$) and reduced pressure ($P_R$) are approximately the same for all gases.*

This is known as <u>principle of corresponding states</u>. although the word "principle" is used, it is just an  approximation. Here, $T_R$ and $P_R$ are defined as

$$T_R = \frac{T}{T_{cr}} \text{ and } P_R = \frac{P}{P_{cr}}$$

# Comparison of Z factors for several gases:



$Z = \frac{Pv}{RT}$

$T_R = 2.00$

$T_R = 1.50$

$T_R = 1.30$

$T_R = 1.20$

$T_R = 1.10$

$T_R = 1.00$

Reduced pressure $P_R$

Legend:

× Methane   ■ Iso-pentane
○ Ethylene   ◔ n-Heptane
▲ Ethane   △ Nitrogen
○ Propane   ◉ Carbon dioxide
□ n-Butane   ● Water

Average curve based on data on hydrocarbons

Ref. Cengel and Boles , 8th Edition (2015)
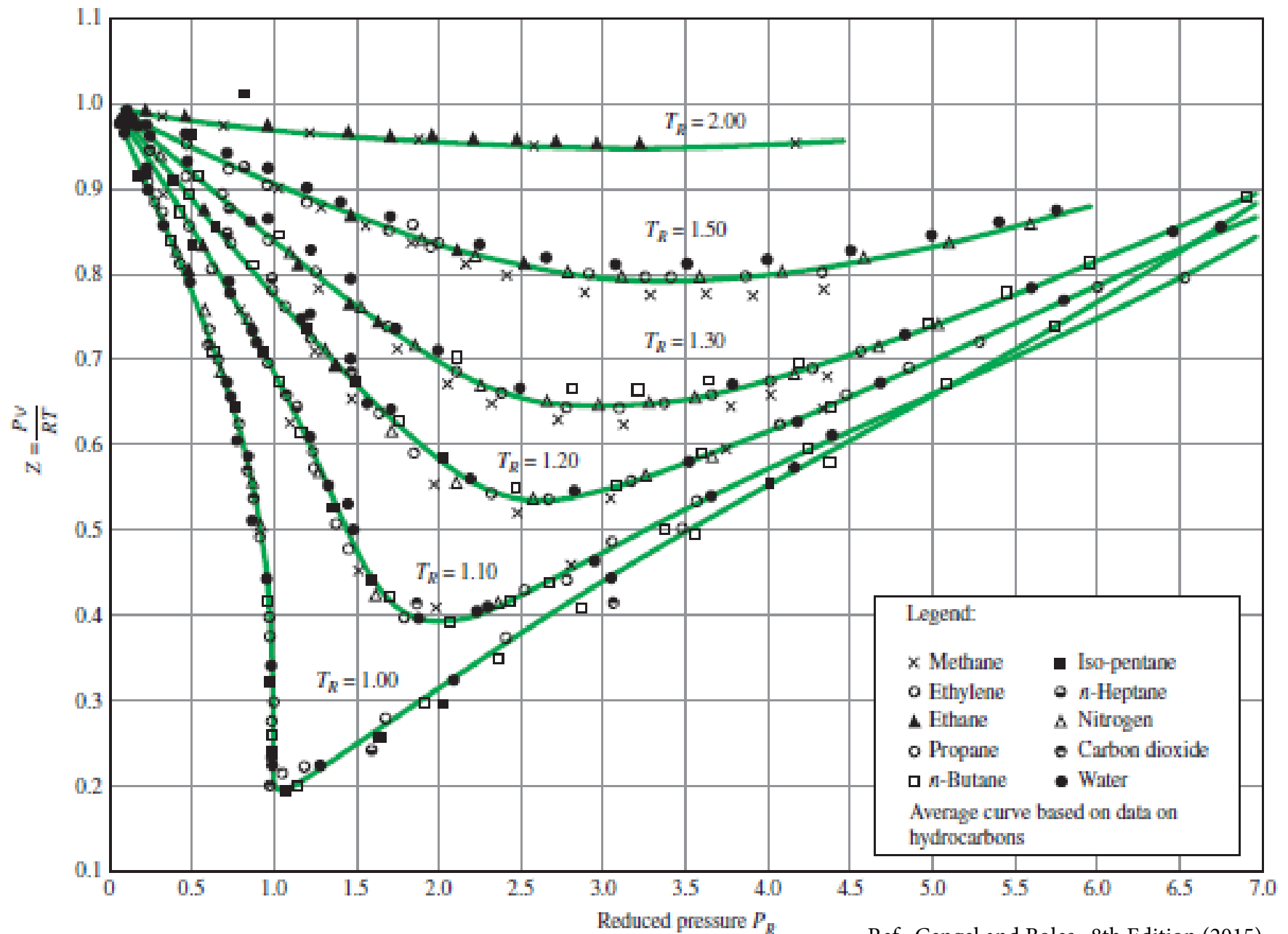
## Comparison of Z factors for several gases:

Based on the experimental values of Z plotted on previous slide, it can be observed that :

(1) At very low pressures ($P_R \ll 1$) gas behaves as ideal gas irrespective of temperature

(2) At $T_R > 2$, ideal gas behavior can be assumed with good accuracy except when $P_R \gg 1$

(3) The deviation from ideal gas behavior is the greatest in the vicinity of critical point ($T_R = 1$, $P_R = 1$)

# Generalized compressibility chart :



(a) $0 < P_r < 1.0$

$T_r = 5.00$
3.00
2.00
1.60
1.40
1.30
1.20
1.15
1.10
1.05
$v_r = 0.07$
$T_r = 1.0$

**Compressibility Factor, $Z = \dfrac{Pv}{RT}$**

**Reduced Pressure, $P_r$**

Note    $T_r = 2.5$    $Z = 1.00$
$T_r = 15 = T_r = 3.00$

... Deviation > 1.0%

**Nelson—Obert**
**Generalized**
**Compressibility Charts**

Reduced pressure $P_r = \dfrac{P}{P_{cr}}$

Reduced temperature $T_r = \dfrac{T}{T_{cr}}$

Pseudo reduced volume $v_r = \dfrac{v}{RT_{cr}/P_{cr}}$

Chart No: 1

1953

Ref. Cengel and Boles , 8th Edition (2015)

# Generalized compressibility chart :



(b) $0 < P_r < 7$

Nelson—Obert
Generalized
Compressibility Charts

Reduced pressure $P_r = \dfrac{P}{P_{cr}}$

Reduced temperature $T_r = \dfrac{T}{T_{cr}}$

Pseudo reduced volume $v_r = \dfrac{v}{RT_{cr}/P_{cr}}$

Chart No: 2

1953

Compressibility Factor, $Z = \dfrac{Pv}{RT}$

Reduced pressure, $P_r$

Ref. Cengel and Boles , 8th Edition (2015)

# Example :

Determine the specific volume of refrigerant-134a at 1 MPa and 50°C, using (a) the ideal-gas equation of state and (b) the generalized compressibility chart. Compare the values obtained to the actual value of 0.021796 m³/kg and determine the error involved in each case.

**SOLUTION** The specific volume of refrigerant-134a is to be determined assuming ideal- and nonideal-gas behavior.

*Analysis* The gas constant, the critical pressure, and the critical temperature of refrigerant-134a are determined from Table A–1 to be

$$R = 0.0815 \text{ kPa·m}^3/\text{kg·K}$$

$$P_{cr} = 4.059 \text{ MPa}$$

$$T_{cr} = 374.2 \text{ K}$$

(a) The specific volume of refrigerant-134a under the ideal-gas assumption is

$$v = \frac{RT}{P} = \frac{(0.0815 \text{ kPa·m}^3/\text{kg·K})(323 \text{ K})}{1000 \text{ kPa}} = \textbf{0.026325 m}^3\textbf{/kg}$$

Therefore, treating the refrigerant-134a vapor as an ideal gas would result in an error of (0.026325 − 0.021796)/0.021796 = 0.208, or 20.8 percent in this case.

Ref. Cengel and Boles , 8th Edition (2015)

# Example :

(b) To determine the correction factor $Z$ from the compressibility chart, we first need to calculate the reduced pressure and temperature:

$$\left. \begin{array}{l} P_R = \dfrac{P}{P_{cr}} = \dfrac{1\ \text{MPa}}{4.059\ \text{MPa}} = 0.246 \\[3mm] T_R = \dfrac{T}{T_{cr}} = \dfrac{323\ \text{K}}{374.2\ \text{K}} = 0.863 \end{array} \right\} \quad Z = 0.84$$

Thus

$$v = Zv_{\text{ideal}} = (0.84)(0.026325\ \text{m}^3/\text{kg}) = \mathbf{0.022113\ m^3/kg}$$

**Discussion** The error in this result is less than **2 percent**. Therefore, in the absence of tabulated data, the generalized compressibility chart can be used with confidence.

Note that the Z value reported above can be read from the generalized compressibility chart given on slide 10.

Ref. Cengel and Boles , 8th Edition (2015)