



Module

3

Lecture
6

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Thermodynamics

Properties of Pure Substances

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Properties of Pure Substances

(Contd...)

Ideal Gas

- Any equation that relates the pressure, temperature, and specific volume of a substance is called an *equation of state*.
- Property relations that involve other properties of a substance at equilibrium states are also referred to as *equations of state*.
- There are several equations of state, some simple and others very complex.
- The simplest and best-known equation of state for substances in the gas phase is the ideal-gas equation of state.
- This equation predicts the P - v - T behaviour of a gas quite accurately within some properly selected region.
- *Gas and vapor* are often used as synonymous words.
- The vapor phase of a substance is customarily called a *gas* when it is above the critical temperature.

In 1802, J. Charles and J. Gay-Lussac, Frenchmen, experimentally determined that at low pressures the volume of a gas is proportional to its temperature. That is,

$$Pv = RT$$

where the constant of proportionality R is called the *gas constant*. This equation is called *the ideal-gas equation of state*, or simply the *ideal-gas relation*, and a gas that obeys this relation is called an *ideal gas*. In this equation, P is the absolute pressure, T is the absolute temperature, and v is the specific volume. The gas constant R is different for each gas and is determined from

$$R = \frac{R_u}{M} \quad (\text{kJ/kg} \cdot \text{K or kPa} \cdot \text{m}^3/\text{kg} \cdot \text{K})$$

where R_u is the *universal gas constant* and M is the molar mass (also called *molecular weight*) of the gas. The constant R_u is the same for all substances, and its value is

$$R_u = \begin{cases} 8.314 \text{ kJ/kmol} \cdot \text{K} \\ 8.314 \text{ kPa} \cdot \text{m}^3/\text{kmol} \cdot \text{K} \\ 0.08314 \text{ bar} \cdot \text{m}^3/\text{kmol} \cdot \text{K} \\ 1.986 \text{ Btu/lbmol} \cdot \text{R} \\ 10.73 \text{ psia} \cdot \text{ft}^3/\text{lbmol} \cdot \text{R} \\ 1545 \text{ ft} \cdot \text{lbf/lbmol} \cdot \text{R} \end{cases}$$

- An ideal gas is an *imaginary* substance that obeys the relation $Pv=RT$.
- It has been experimentally observed that the ideal-gas relation given closely approximates the P - v - T behaviour of real gases at low densities.
- At low pressures and high temperatures, the density of a gas decreases, and the gas behaves as an ideal gas under these conditions.

- In the range of practical interest, many familiar gases such as air, nitrogen, oxygen, hydrogen, helium, argon, neon, krypton, and even heavier gases such as carbon dioxide can be treated as ideal gases with negligible error (often less than 1 percent).
- Dense gases such as water vapor in steam power plants and refrigerant vapor in refrigerators, however, should not be treated as ideal gases. Instead, the property tables should be used for these substances.

Is Water Vapor an Ideal Gas?

- At pressures below 10 kPa, water vapor can be treated as an ideal gas, regardless of its temperature, with negligible error (less than 0.1 percent).
- At higher pressures, however, the ideal-gas assumption yields unacceptable errors, particularly in the vicinity of the critical point and the saturated vapor line (over 100 percent).
- Therefore, in air-conditioning applications, the water vapor in the air can be treated as an ideal gas with essentially no error since the pressure of the water vapor is very low.
- In steam power plant applications, however, the pressures involved are usually very high; therefore, ideal-gas relations should not be used.

Compressibility factor—a measure of deviation from ideal-gas behaviour

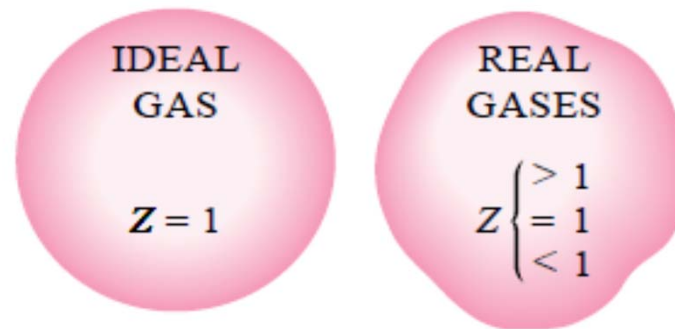
- The ideal-gas equation is very simple and thus very convenient to use. But, gases deviate from ideal-gas behaviour significantly at states near the saturation region and the critical point.
- This deviation from ideal-gas behaviour at a given temperature and pressure can accurately be accounted for by the introduction of a correction factor called the *compressibility factor* Z defined as

$$Z = \frac{Pv}{RT} \quad \text{or,} \quad Pv = ZRT$$

It can also be expressed as

$$Z = \frac{v_{\text{actual}}}{v_{\text{ideal}}}$$

Where $v_{\text{ideal}} = RT/P$. Obviously, $Z=1$ for ideal gases. For real gases Z can be greater than or less than unity. The farther away Z is from unity, the more the gas deviates from ideal-gas behaviour.



The following observations can be made from the generalized compressibility chart:

1. At very low pressures ($P_R \ll 1$), the gases behave as an ideal gas regardless of temperature (Fig. 3.26),
2. At high temperatures ($T_R > 2$), ideal-gas behaviour can be assumed with good accuracy regardless of pressure (except when $P_R \gg 1$).
3. The deviation of a gas from ideal-gas behaviour is greatest in the vicinity of the critical point (Fig. 3.27).

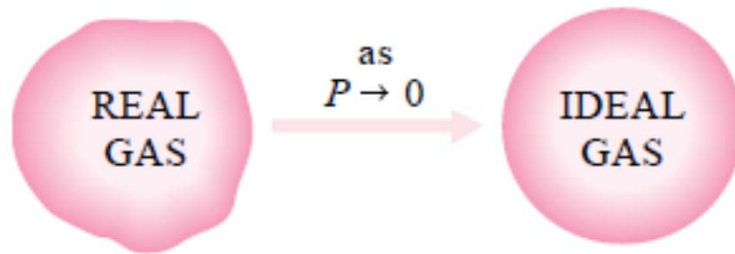


Fig. 3.26: At very low pressures, all gases approach ideal-gas behaviour (regardless of their temperature).

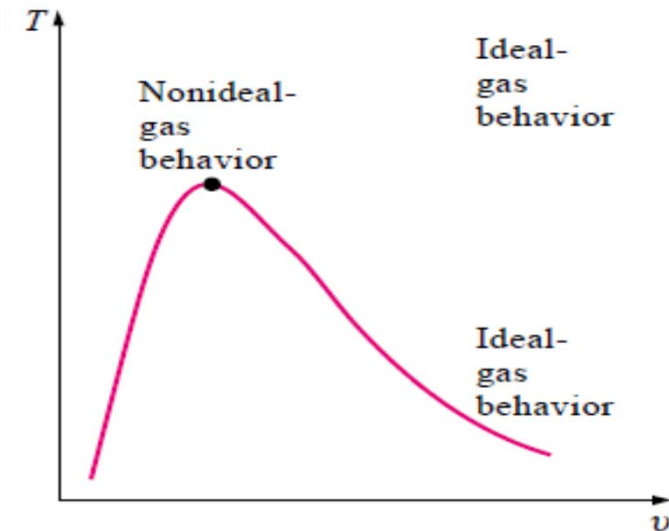


Fig. 3.27: Gases deviate from the ideal-gas behaviour most in the neighbourhood of the critical point.

Van der Waals proposed the following equation of state for a real gas

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

where a and b are constants. The above equation is known as van der Waals equation of state. The term a/v^2 accounts for the intermolecular forces, and b accounts for the volume occupied by the gas molecules.

The term a/v^2 is called the force of cohesion, whereas the constant b is known as co-volume.

Virial Equation of State

The equation of state of a substance can also be expressed in a series form as

$$P = \frac{RT}{v} + \frac{a(T)}{v^2} + \frac{b(T)}{v^3} + \frac{c(T)}{v^4} + \frac{d(T)}{v^5} + \dots$$

This and similar equations are called the *virial equations of state*, and the coefficients $a(T)$, $b(T)$, $c(T)$, and so on, that are functions of temperature alone are called *virial coefficients*.

Specific Heats, Internal Energy and Enthalpy

The specific heat or heat capacity of a substance (C) is the amount of heat required to change temperature of the unit mass of the substance by one degree. Then,

$$C = \frac{1}{m} \left(\frac{\partial Q}{\partial T} \right) = \frac{\partial q}{\partial T}$$

- The unit of specific heat in SI system is J/kg-K (or kJ/kg-K).
- In general, this energy needed to change the temperature depends on how the process is executed.
- In thermodynamics, we are interested in two kinds of specific heats, namely *specific heat at constant volume (C_v)* and *specific heat at constant pressure (C_p)*.

- Physically, *specific heat at constant volume* (C_v) is defined as the energy required to raise the temperature of the unit mass of a substance by one degree as the volume is maintained constant.
- The energy required to do the same as the pressure is maintained constant is *specific heat at constant pressure* (C_p).
- The C_p is always greater than C_v because at constant pressure the system is allowed to expand and the energy for this expansion work must also be supplied to the system.

According to the state -postulate we know that the state of a simple compressible substance is completely specified by two independent, intensive properties. Consider the specific internal energy to be a function of temperature and specific volume, that is

$$u = u(T, v)$$

Using the chain rule, we can write

$$du = \left. \frac{\partial u}{\partial T} \right|_v dT + \left. \frac{\partial u}{\partial v} \right|_T dv$$

The *specific heat at constant volume* (C_v) is defined as

$$C_v = \left. \frac{\partial u}{\partial T} \right|_v$$

It has been demonstrated mathematically and experimentally that for an ideal gas both the internal energy and enthalpy is a function of the temperature only. That is for an ideal gas

$$\left. \frac{\partial u}{\partial v} \right|_T = 0$$

Combining above equations, we have

$$du = C_v dT$$

Similar to internal energy, considering specific enthalpy to be a function of temperature and pressure, we have

$$h = h(T, P)$$

Using the chain rule, we can write

$$dh = \left. \frac{\partial h}{\partial T} \right|_p dT + \left. \frac{\partial h}{\partial p} \right|_T dp$$

The *specific heat at constant pressure* (C_p) is defined as

$$C_p = \left. \frac{\partial h}{\partial T} \right|_p$$

For an ideal gas both the internal energy and enthalpy is a function of the temperature only. That is for an ideal gas

$$\left. \frac{\partial h}{\partial p} \right|_T = 0$$

Combining above equations, we have

$$dh = C_p dT$$

The change in internal energy or enthalpy for an ideal gas during a process from state 1 to state 2 is determined by integrating these equations:

$$\Delta u = u_2 - u_1 = C_v(T_2 - T_1)$$

and

$$\Delta h = h_2 - h_1 = C_p(T_2 - T_1)$$

Specific heat relations of ideal gases

Enthalpy of a substance is a combination of properties.

$$h = u + Pv$$

From equation of state for an ideal gas, we can write

$$Pv = RT$$

Then, we can write

$$h = u + RT$$

Writing in differential forms

$$dh = du + d(RT)$$

$$dh = du + RdT$$

From the specific heat relations for an ideal gas, we have

$$dh = C_p dT \quad \text{and} \quad du = C_v dT$$

From the specific heat relations for an ideal gas, we have

$$C_p = C_v + R$$

It is evident from above equation that although C_p and C_v for ideal gases are function of temperatures only, the difference between them is always a constant (since R is constant).

The specific heat ratio, γ is defined as

$$\gamma = \frac{C_p}{C_v}$$

From above equations, we have

$$C_p = \frac{\gamma R}{\gamma - 1} \quad \text{and} \quad C_v = \frac{R}{\gamma - 1}$$

For air, $C_p = 1.005 \text{ kJ/kg.K}$ and $C_v = 0.718 \text{ kJ/kg.K}$

Thank You