Thermodynamics
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Lecture 42
Beyond Ideal Gases - Part 1

In the previous lecture, we covered concepts of ideal gas and a mixture of ideal gases. Let's look at the case where the gas is not ideal.

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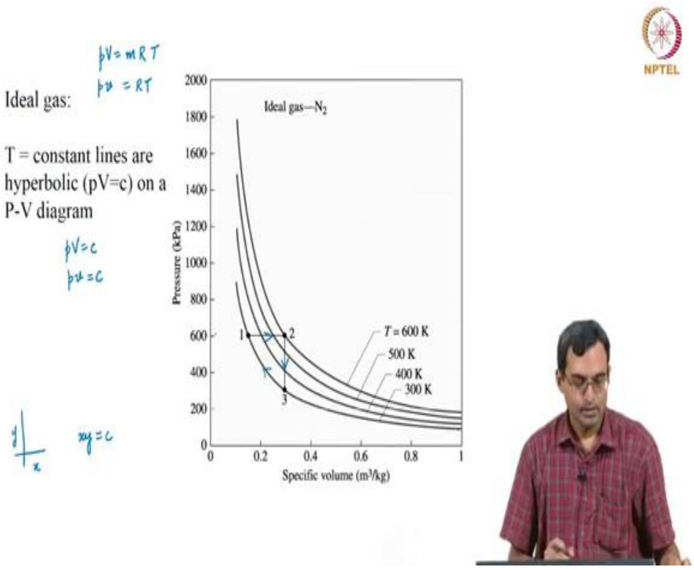

Figure 1.

We know, for an ideal gas, $pV = mRT$ or $pv = RT$, where p, V, m, R, T and v represent pressure, volume, mass, specific gas constant, temperature and specific volume of the gas. For an isothermal process, $pV = constant$ as R is constant for a gas and m is fixed for a system. Also, $pv = constant$. On a p-V diagram, pV=constant represent a rectangular hyperbola. Similarly, on a p-v diagram, pv=constant represent a rectangular hyperbola (see Fig. 1). As the temperature increases, the value of the constant in pv = constant increases, and we get different curves (isotherms) (see Fig. 1). For the process 1-2 (Fig. 1), which is an isobaric process, the specific volume (and the volume) increases along with temperature (temperature increases from 300 K to 600 K). For the process 2-3 (Fig. 1), the specific volume (and volume) is constant, but the pressure as well as the temperature decreases (temperature decreases from 600 K to 300 K). For the process 3-1 along the isotherm, the temperature remains constant (T=300 K), but the specific volume decreases and the pressure increases.

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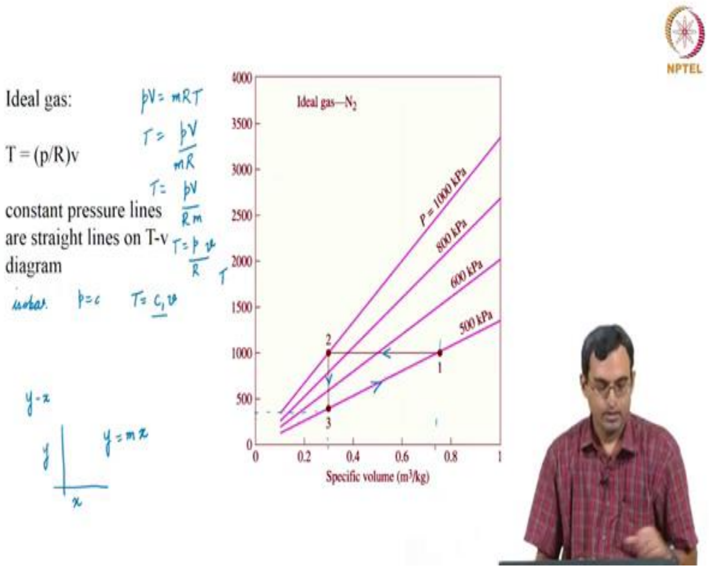

Figure 2.

The ideal gas equation can also be written as $T = \frac{pv}{R}\left(or\ T = \frac{pV}{mR}\right)$. If, for a process, p=constant, then T=constant×v, which is a straight line with slope $\frac{p}{R}$ passing through the origin on a T-v diagram (see Fig. 2). For a larger value of p, the slope is also higher (Fig. 2). Different isobars are shown in Fig. 2. For the process 1-2 (Fig. 2), the temperature is constant, but the specific volume decreases and the pressure increases (pressure increases from 500 kPa to 1000 kPa). For the process 2-3, the specific volume is constant, but the temperature as well as the pressure decreases (pressure decreases from 1000 kPa to 500 kPa). For the process 3-1, the pressure stays constant as it happens along an isobar p=500 kPa, but the specific volume and the temperature increase.

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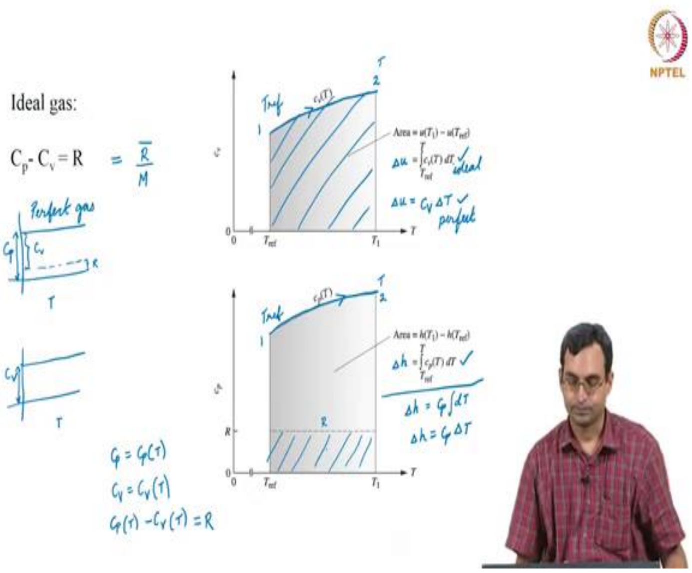

Figure 3.

For an ideal gas, $C_p - C_v = R$ where $R = \frac{\bar{R}}{M}$. Here, R is the specific gas constant, $\bar{R}$ is the universal gas constant, M is the molecular weight. For a perfect gas, C_p and C_v are constants. C_p and C_v versus T are lines parallel to the T axis. Hence, $C_p - C_v$ is always constant which is R. For an ideal gas, C_p and C_v are functions of temperature [they can be represented as $C_p(T)$ and $C_v(T)$]. As temperature increases, both, $C_p(T)$ and $C_v(T)$, tend to increase. However, the difference, $C_p(T) - C_v(T)$, stays the same which is R. Figure 3 shows the variation of C_p and C_v with temperature (from T_{ref} to T_1). For an ideal gas, $\Delta u = \int C_v(T)dT =$ change in specific internal energy = area under the curve. For a prefect gas, C_v is constant. Hence, $\Delta u = C_v\Delta T$. Similarly, for an ideal gas, $\Delta h = \int C_p(T)dT =$ change in specific enthalpy. Again, for a perfect gas, $\Delta h = C_p\Delta T$.

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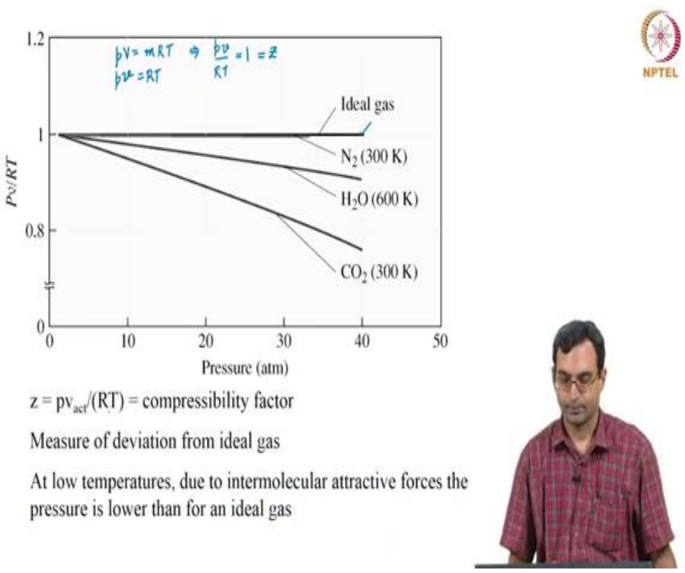

Figure 4.

For an ideal gas, $pv = RT$ or $\frac{pv}{RT} = 1$. The ratio $\frac{pv}{RT}$ is called as Z, the compressibility factor, which has a value of 1 for an ideal gas. For a real gas, Z does not have to be 1. For an ideal gas, the value of Z is 1 irrespective of the value of pressure (Fig. 4). For nitrogen at T=300 K, the value of Z is close to 1 over pressures from p=0 atm to p=40 atm. It means that nitrogen behaves as an ideal gas at these conditions. The Z value for water vapor at T=600 K deviates from 1 as the pressure increases (Fig. 4). Similar conclusion can be drawn in the case of carbon dioxide (Fig. 4). Hence, these gases cannot be considered as ideal gases at these conditions. The value of Z is the measure of deviation of the behavior of a gas from the ideal gas behavior.

There are some reasons why gases do not behave in ideal fashion. At low temperatures, due to intermolecular attractive forces, the pressure is lower than for an ideal gas. Also, the volume occupied would be smaller than for the ideal gas.

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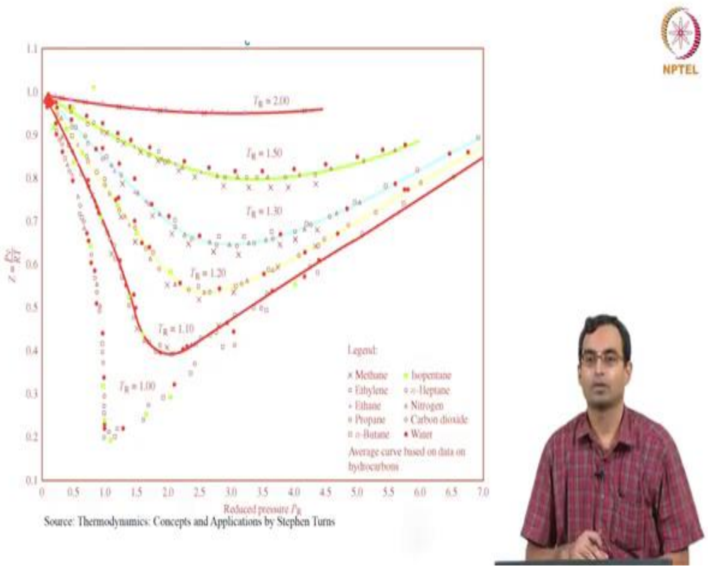

How to deal with real gases? One way is use compressibility charts which we will study in the next class.