

Example 1

Determine \bar{v} for $\text{H}_2\text{O}(\text{g})$ at $P = 140$ bars and $T = 673$ K using the ideal gas equation, the compressibility chart, the steam tables and the VW equation of state. What is the size of a single molecule?

Solution

- Ideal gas.

$$\bar{v} = \bar{R}T/P = 0.08314 \text{ bar m}^3 \text{ kmole}^{-1} \text{ K}^{-1} \times 673 \text{ K} \div 140 \text{ bar} = 0.4 \text{ m}^3 \text{ kmole}^{-1}.$$

- Compressibility chart.

$$P_R = P/P_c = 140 \text{ bar} \div 220.9 \text{ bar} = 0.634,$$

$$T_R = T/T_c = 673 \text{ K} \div 647.3 \text{ K} = 1.04. \text{ From the compressibility chart, } Z = 0.78.$$

$$\text{Since } P\bar{v} = Z\bar{R}T,$$

$$\bar{v} = 0.78 \times 0.08314 \text{ bar m}^3 \text{ kmole}^{-1} \text{ K}^{-1} \times 673 \text{ K} \div 140 \text{ bar} = 0.312 \text{ m}^3 \text{ kmole}^{-1}.$$

- Tables.

$$\bar{v} = 17.22 \text{ cm}^3 \text{ g}^{-1} \times 10^{-6} \text{ m}^3 \text{ cm}^{-3} \times 10^3 \text{ g kg}^{-1} \div 18.02 \text{ kg kmole}^{-1} = 0.31 \text{ m}^3 \text{ kmole}^{-1}.$$

- Van der Waals equation.

$$\bar{a} = 27 \bar{R}^2 T_c^2 / 64 P_c = 27 \times 0.08314^2 \text{ bar}^2 \text{ m}^6 \text{ kmole}^{-2} \text{ K}^{-2} \div 647.3^2 \text{ K}^2 \div (64 \times 220.9 \text{ bar}), \text{ i.e.,}$$

$$\bar{a} = 5.531 \text{ bar m}^6 \text{ kmole}^{-2}.$$

$$\text{Likewise, } \bar{b} = \bar{R}T_c / (8P_c) = (0.08314 \text{ bar m}^3 \text{ kmole}^{-1} \text{ K}^{-1} \times 647.3 \text{ K}) \div (8 \times 220.9 \text{ bar}), \text{ i.e.,}$$

$$\bar{b} = 0.0305 \text{ m}^3 \text{ kmole}^{-1}.$$

However, at 140 bar, $T = 673$ K, $\bar{v} = 0.31 \text{ m}^3 \text{ kmole}^{-1}$, according to VW equation. (Note that use of this equation produces a closer prediction to the tabulated value than was obtained using the ideal gas law.)

- Molecular diameter

Recall that \bar{b} represents the finite volume or $4 \times$ (body volume) of the molecules. A kmole contains 6.023×10^{26} molecules. Therefore, the body volume of a single molecule $\approx 0.0305 \text{ m}^3 \text{ kmole}^{-1} \div (4 \times 6.023 \times 10^{26} \text{ molecules}) = 1.264 \times 10^{-28} \text{ m}^3$.

The molecular volume

$$\pi d^3 / 6 = 1.264 \times 10^{-29} \text{ m}^3, \text{ i.e., } d = 2.89 \times 10^{-10} \text{ m} = 2.89 \text{ \AA}.$$

Remarks

- The term $-\bar{a}/\bar{v}^2$ in the VW equation corresponds to the reduction in pressure due to intermolecular forces. When $\bar{v} = 0.31 \text{ m}^3 \text{ kmole}^{-1}$, $-\bar{a}/\bar{v}^2 = -57.6 \text{ bar}$, while the first term $\bar{R}T/(\bar{v}-\bar{b}) = 199.5 \text{ bar}$. This implies that the frequent molecular collisions create a pressure of 199.5 bars, but due to the strong attraction forces in the dense gas phase the molecules are pulled back together with a pressure equivalent of 57.6 bar. Therefore, the net pressure is 141.9 bar.
- Since $\sigma = \{(6/\pi)(\bar{b}/4)/N_{\text{Avog}}\}^{1/3}$, and $\bar{b} = (1/8)\bar{R}T_c/P_c$ using the VW equation of state, $\sigma = \{(6/32\pi)\bar{R}T_c/(P_c N_{\text{Avog}})\}^{1/3} = 0.391(k_B T_c/P_c)^{1/3}$. Using the value $k_B = 1.3804 \times 10^{-26} \text{ kJ K}^{-1} \text{ molecule}^{-1}$, $\sigma = 2.02(T_c(\text{K})/P_c)^{1/3} \text{ \AA}$ with P_c expressed in bar. For instance, if $T_c = 647 \text{ K}$ and $P_c = 221 \text{ bar}$, $\sigma = 2.89 \text{ \AA}$.

Example 2

Determine the value of v and compare it with that obtained from the steam tables, the value of v'_R , and that of Z_{RK} for water at a pressure of 250 bars and a temperature of 600°C.

Solution

For water $P_c = 220.9$, and $T_c = 647.3$ K. Using Eq. (41)

$$\bar{a} = 0.42748 \bar{R}^2 T_c^{2.5} / P_c = 0.42748 \times (0.08314 \text{ bar m}^3 \text{ kmole}^{-1} \text{ K}^{-1})^2 \times (647.3 \text{ K})^{2.5} \div 220.9 \text{ bar}$$
$$= 142.59 \text{ bar m}^6 \text{ K}^{1/2} \text{ kmole}^{-2}$$

$$\bar{b} = 0.08664 \bar{R} T_c / P_c = 0.08664 \times 0.08314 \text{ bar m}^3 \text{ kmole}^{-1} \text{ K}^{-1} \times 647.3 \text{ K} \div 220.9 \text{ bar}$$
$$= 0.0211 \text{ m}^3 \text{ kmole}^{-1}.$$

Therefore, for RK

$$250 \text{ bar} = (0.08314 \text{ bar m}^3 \text{ kmole}^{-1} \text{ K}^{-1} \times 873 \text{ K}) \div (\bar{v} - 0.0211) - 142.59 \text{ bar m}^6 \div (873^{1/2} \bar{v} (\bar{v} + 0.0211)).$$

Solving for \bar{v} , we obtain three real solutions. Selecting the largest of the three values, which corresponds to a vapor-like solution, $\bar{v} = 0.246 \text{ m}^3 \text{ kmole}^{-1}$.

$$\therefore v = 0.246 \text{ m}^3 \text{ kmole}^{-1} \div 18.02 \text{ kg kmole}^{-1} = 0.01361 \text{ m}^3 \text{ kg}^{-1}.$$

The steam tables give a value of 0.014137, a difference of -3.7%.

$$v'_c = T_c/P_c = 0.08314 \text{ bar m}^3 \text{ kmole}^{-1} \text{ K}^{-1} \times 647.3 \text{ K} \div 220.9 \text{ bars} = 0.244 \text{ m}^3 \text{ kmole}^{-1}.$$

Since, $v'_R = \bar{v}/v'_c = 0.246 \div 0.244 = 1.008$, and $P_R = 1.132$, $T_R = 1.349$, using Eq. (43), $v'_R = 1.008$.

Now, $(P\bar{v})_{RK} = Z_{RK} \bar{R} T$. Since, $\bar{v}_{RK} = 0.246 \text{ m}^3 \text{ kmole}^{-1}$,

$$Z_{RK} = 250 \text{ bar} \times 0.246 \text{ m}^3 \text{ kmole}^{-1} \div (0.08314 \text{ bar m}^3 \text{ kmole}^{-1} \text{ K}^{-1} \times 873 \text{ K}) = 0.845.$$

Remarks

The reduced parameters $P_R = P/P_c = 250 \div 220.9 = 1.132$, and $T_R = T/T_c = 873 \div 647.3 = 1.349$. A value of $v'_R = 1.007$ can be obtained using Eq. (43). Thereafter, since $v'_c = 0.244$, $\bar{v} = 0.246 \text{ m}^3 \text{ kmole}^{-1}$.

Example 3

Water is compressed isentropically from 0.1 bar and 30°C to 60 bar. Determine the change in volume, and work required to compress the fluid. Treat water as a compressible substance, and assume that at 30°C, $\beta_P = 2.7 \times 10^{-4} \text{ K}^{-1}$, $\beta_T = 44.8 \times 10^{-6} \text{ bar}^{-1}$, $v = 0.00101 \text{ m}^3 \text{ kg}^{-1}$, and $c_p = 4.178 \text{ kJ kg}^{-1} \text{ K}^{-1}$.

Solution

Since $\beta_P = 44.8 \times 10^{-6} \text{ bar}^{-1}$ and $dv = -\beta_P dP$, $\ln v_2/v = -\beta_T (P_2 - P_1) = -0.00268$, i.e., $v_2/v = 0.997$.

Now, $v_2 = 0.997 \times 0.00101 = 0.001007 \text{ m}^3 \text{ kg}^{-1}$, so that

$$v_2 - v = 0.001007 - 0.001010 = 0.000997 \text{ m}^3 \text{ kg}^{-1}.$$

$\delta w = -v dP$ (for a reversible process in an open system).

$$\therefore \delta w = -v (dP/dv) dv = (1/\beta_T) dv.$$

Integrating this expression,

$$w = (1/\beta_T)(v_2 - v) = 100 \text{ kPa bar}^{-1} \times (0.001007 - 0.001010) \div 44.8 \times 10^{-6} = -6.76 \text{ kJ kg}^{-1}.$$