Problem 1.1 Solution

We will need the following unit conversions:

$$1 \text{ ft} = 0.3048 \text{ m}, \qquad 1 \text{ lb} = 0.454 \text{ kg}, \qquad 1 \text{ lbmol} = 454 \text{ mol}$$

(Note on the conversion mol to lbmol: one mol has a mass equal to the molecular weight in g, while one lbmol has a mass equal equal to the molecular weight in lb.) We also need the molar mass of ammonia which is

$$M_m = 17 \text{ g/mol} = 17 \times 10^{-3} \text{ kg/mol}$$

a) Specific Volume:

$$V = \frac{1}{41.3 \text{ lb/ft}^3} = 0.02421 \text{ ft}^3/\text{lb} = 0.00151 \text{ m}^3/\text{kg} = 1.51 \text{ cm}^3/\text{g}$$

b) Molar Volume

$$V_{\text{molar}} = V M_m = 2.567 \times 10^{-5} \text{ m}^3/\text{mol} = 25.67 \text{ cm}^3/\text{mol} = 0.4116 \text{ ft}^3/\text{lb-mol}$$

Problem 1.2 Solution First we write the given equation as

$$T_K = \frac{B}{A - (\ln P_{\text{bar}})/(\ln 10)} - C$$

where T_K refers to T in kelvin, P_{bar} refers to pressure in bar, and the logarithm is natural. Next we use

$$T_F = 1.8(T_K - 273.15) + 32 \quad \text{and} \quad P_{\text{bar}} = \frac{P_{\text{psi}}}{14.5}$$

and substitute these values into the above equation. After some manipulation the result is

$$T_F = \frac{B(1.8)(\ln 10)}{A \ln 10 + \ln(14.5) - \ln P_{\text{psi}}} - C(1.8) - (1.8)(273.15) + 32$$

Doing the algebra,

$$T_F = \frac{5062.37}{13.2153 - \ln P_{\text{psi}}} - 302.217$$

Therefore,

$$A' = 13.2153, \quad B' = 5062.37 \quad C' = 302.217$$

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Problem 1.3 Solution a) The mean velocity is

$$\bar{v} = \left(\frac{8k_B T}{\pi m} \right)^{1/2}$$

where $k_B = 1.38 \times 10^{-23}$ J/K, $T = 273.16$ K. The mass of the water molecule is

$$m = \frac{M_m}{N_{AV}} = \frac{18 \times 10^{-3} \text{ kg/mol}}{6.022 \times 10^{23} \text{ mol}^{-1}} = 2.98904 \times 10^{-26} \text{ kg}.$$

The mean velocity is

$$\bar{v} = 566.699 \text{ m/s} = 2040.12 \text{ km/h} = 1267 \text{ mph}$$

This result depends only on temperature and since all three phases are the same temperature, molecules have the same mean velocity in all three phases.

b) The mean kinetic energy is

$$\bar{E}_{kin} = \overline{\tfrac{1}{2}mv^2} = \tfrac{1}{2}m\overline{v^2}$$

where $\overline{v^2}$ is the mean squared velocity,

$$\overline{v^2} = \frac{3k_B T}{m}.$$

With this the mean kinetic energy is

$$\bar{E}_{kin} = \frac{3}{2}k_B T = 5.65441 \times 10^{-21} \text{ J}$$

This is the mean kinetic energy per molecule in all phases. The number of molecules in 1 kg of water is

$$N = \frac{1 \text{ kg}}{18 \times 10^{-3} \text{ kg/mol}} 6/022 \times 10^{23} = 3.34556 \times 10^{25}$$

The total kinetic energy in 1 kg of water at 0.01 °C (regardless of phase) is

$$\bar{E}_{kin} = \left(5.65441 \times 10^{-21} \text{ J} \right) \left(3.34556 \times 10^{25} \right) = 189,171 \text{ J} = 189 \text{ kJ}$$

Comment: This is the *translational* kinetic energy of the molecule, i.e., the kinetic energy due to the motion of the center of mass. A water molecule possesses additional forms of kinetic energy that arise from the rotation of the molecule, the bending of bonds, and the vibration of oxygen and hydrogen atoms about their equilibrium positions. These are not included in this calculation as the Maxwell-Boltzmann distribution refers specifically to the translational kinetic energy.

c) The above calculation shows that the mean kinetic energy depends *only on temperature* (it is independent of pressure or of the mass of the molecule). Therefore, oxygen at 0.01 °C has the same kinetic energy as water at the same temperature:

$$\bar{E}_{kin} = \frac{3}{2}k_B T = 5.65441 \times 10^{-21} \text{ J}$$

Problem 1.4 Solution
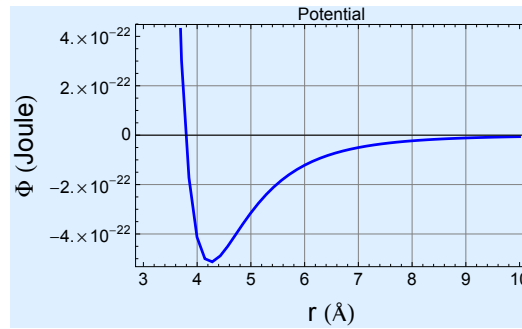
Potential

a) The potential has a minimum just above 4 Å or so. To determine this value accurately we must set the derivative of the potential equal to zero solve for the value of r. To do this easily, we define a new variable $x = r/\sigma$ and rewrite the potential as:

$$\Phi = a\left(x^{-12} - x^{-6}\right)$$

By chain rule we now have:

$$\frac{dF}{dr} = \frac{dF}{dx}\frac{dx}{dr} = \left(-12x^{-13} + 6x^{-7}\right)\frac{dx}{dr}$$
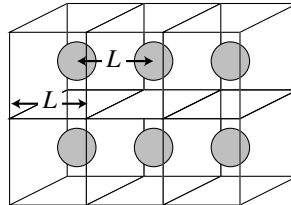
Setting this to zero and solving for x we have:

$$-12x^{-13} + 6x^{-7} = 0 \quad \Rightarrow \quad x = 2^{1/6}$$

Since $r = \sigma x$, the value of r that minimizes the potential is

$$r_* = 2^{1/6}\sigma = (4.24964)(3.786\ \text{Å}) = 4.25\ \text{Å}$$

b) If we imagine N molecules to be situated at the center of cubes whose sides are equal to r_*,

the volume occupied is

$$V = N(r_*)^3$$

These N molecules correspond to N/N_{Av} mol and their total mass is

$$M = \frac{N}{N_{\text{AV}}}M_m$$

where M_m is the molar mass of methane ($M_m = 16 \cdot 10^{-3}$ kg/mol). For the density, therefore, we obtain the following final formula:

$$\rho = \frac{M_m}{N_{\text{AV}}(r_*)^3}$$

By numerical substitution we finally obtain the density:

$$\rho = \frac{16 \cdot 10^{-3}\ \text{kg/mol}}{(6.024 \cdot 10^{23}\ \text{mol}^{-1})(4.25\ \text{Å})(10^{-10}\ \text{m/Å})} = 346\ \text{kg/m}^3 = 0.346\ \text{g/cm}^3$$

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