Problem 2-7

If n moles of an ideal gas at the temperature 4 K can be pumped through a tube of diameter d, what must be the diameter of the tube to pump the same number of moles of gas at the temperature 300 K?

Solution

We should assume that the pressure and the length of the tube is the same in two case, then from $PV = nRT$ we get

$$\frac{V_1}{V_2} = \frac{d_1^2}{d_2^2} = \frac{T_2}{T_1} \quad \Rightarrow \quad d_2 = d_1\sqrt{\frac{T_2}{T_1}} \simeq 8.66d_1$$

Problem 2-14

A vessel contains CO_2 at the temperature of 137 C. The specific volume is 0.07 m^{3}kmol^{-1}.

1. Compute the pressure in Nm^{-2} (a) from the ideal gas equation, (b) from the van der Waals equation.
2. Calculate the ratio $\frac{Pv}{T}$ (in J kmol^{-1}K^{-1}), for the two pressures found above, and compare with experimental value as read from Fig. 2-1 (p. 12 of the lecture notes) assuming that T_2=137 C.

Solution

$$(a): \quad P = \frac{RT}{v} = 4.87 \times 10^7 \frac{N}{m^2}$$

$$(b): \quad P = \frac{RT}{v-b} - \frac{a}{v^2} = 5.1 \times 10^7 \frac{N}{m^2}$$

$$(c): \quad \left(\frac{PV}{T}\right)_{\text{ideal}} = 8.31 \times 10^3 \frac{J}{kmolK}, \qquad \left(\frac{PV}{T}\right)_{\text{VdW}} = 8.7 \times 10^3 \frac{J}{kmolK}$$

Problem 2-25

A substance has compressibility $\kappa = \frac{aT^3}{P^2}$ and expansivity $\beta = \frac{bT^2}{P}$ where a and b are constants. Find the equation of state of the substance and the ratio $\frac{a}{b}$.

Solution #1: consider $\ln V(P_2,T_2) - \ln V(P_1,T_1)$.

Since $\kappa = -\frac{1}{V}\left(\frac{dV}{dP}\right)_T = -\left(\frac{d\ln V}{dP}\right)_T$ and $\beta = \frac{1}{V}\left(\frac{dV}{dT}\right)_P = -\left(\frac{d\ln V}{dT}\right)_P$ we get along the path $P_1,T_1 \to P_2,T_1 \to P_2,T_2$

$$\begin{aligned}\ln V(P_2,T_2) - \ln V(P_1,T_1) &= \ln V(P_2,T_2) - \ln V(P_2,T_1) + \ln V(P_2,T_1) - \ln V(P_1,T_1)\\ = \int_{T_1}^{T_2} dT \left(\frac{d\ln V}{dT}\right)_{P_2} + \int_{P_1}^{P_2}\left(\frac{d\ln V}{dP}\right)_{T_1} &= \int_{T_1}^{T_2} dT\,\frac{bT^2}{P_2} - \int_{P_1}^{P_2} dP\,\frac{aT_1^3}{P^2} = \frac{bT_2^3}{3P_2} - \frac{bT_1^3}{3P_2} + \frac{aT_1^3}{P_2} - \frac{aT_1^3}{P_1}\end{aligned}$$

On the other hand, along the path $P_1,T_1 \to P_1,T_2 \to P_2,T_2$ we have

$$\begin{aligned}\ln V(P_2,T_2) - \ln V(P_1,T_1) &= \ln V(P_2,T_2) - \ln V(P_1,T_2) + \ln V(P_1,T_2) - \ln V(P_1,T_1)\\ = \int_{P_1}^{P_2}\left(\frac{d\ln V}{dP}\right)_{T_2} + \int_{T_1}^{T_2} dT\left(\frac{d\ln V}{\partial T}\right)_{P_1} &= -\int_{P_1}^{P_2} dP\,\frac{aT_2^3}{P^2} + \int_{T_1}^{T_2} dT\,\frac{bT^2}{P_1} = \frac{aT_2^3}{P_2} - \frac{aT_2^3}{P_1} + \frac{bT_2^3}{3P_1} - \frac{bT_1^3}{3P_1}\end{aligned}$$

$\Rightarrow$

$$\frac{1}{P_2}\left(\frac{b}{3}T_2^3 - \frac{b}{3}T_1^3 + aT_1^3\right) - \frac{aT_1^3}{P_1} = \frac{aT_2^3}{P_2} + \frac{1}{P_1}\left(-aT_2^3 + \frac{b}{3}T_2^3 - \frac{b}{3}T_1^3\right) \Leftrightarrow \frac{P_1}{P_2}\left(\frac{b}{3}T_2^3 - \frac{b}{3}T_1^3 + aT_1^3 - aT_2^3\right) = \left(aT_1^3 - aT_2^3 + \frac{b}{3}T_2^3 - \frac{b}{3}T_1^3\right)$$

Since P_1 and P_2 are arbitrary, this can be true only if

$$\frac{b}{3}T_2^3 - \frac{b}{3}T_1^3 + aT_1^3 - aT_2^3 = aT_1^3 - aT_2^3 + \frac{b}{3}T_2^3 - \frac{b}{3}T_1^3 = 0 \quad \Rightarrow \quad a = \frac{b}{3}$$

so the equation of state is

$$\ln V(P_2,T_2) - \ln V(P_1,T_1) = \frac{aT_2^3}{P_2} - \frac{aT_2^3}{P_2} \qquad \Rightarrow \qquad V(P,T) = e^{\frac{aT^3}{P}} \times \text{const}$$

Solution #2: use the fact that β and κ are partial derivatives

$$\begin{aligned}
\kappa &= -\frac{1}{V}\Big(\frac{dV}{dP}\Big)_T = -\frac{1}{V}\frac{\partial V(P,T)}{\partial P} = -\frac{\partial \ln V(P,T)}{\partial P} = \frac{aT^3}{P^2} \\
\beta &= \frac{1}{V}\Big(\frac{dV}{dT}\Big)_P = -\frac{1}{V}\frac{\partial V(P,T)}{\partial T} = \frac{\partial \ln V(P,T)}{\partial T} = \frac{bT^2}{P}
\end{aligned}$$

Calculating indefinite integrals, we get

$$\begin{aligned}
\frac{\partial \ln V(P,T)}{\partial P} &= -\frac{aT^3}{P^2} \Rightarrow \ln V(T,P) = \frac{aT^3}{P} + F_1(T) \\
\frac{\partial \ln V(P,T)}{\partial T} &= \frac{bT^2}{P} \Rightarrow \ln V(T,P) = \frac{bT^3}{3P} + F_2(P)
\end{aligned}$$

where F_1 and F_2 are arbitrary functions. For both of these formulas to be correct, one needs $\frac{a}{b} = \frac{1}{3}$ (and $F_1 = F_2 =$const) so the equation of state is

$$V(P,T) = e^{\frac{aT^3}{P}} \times \text{const}$$