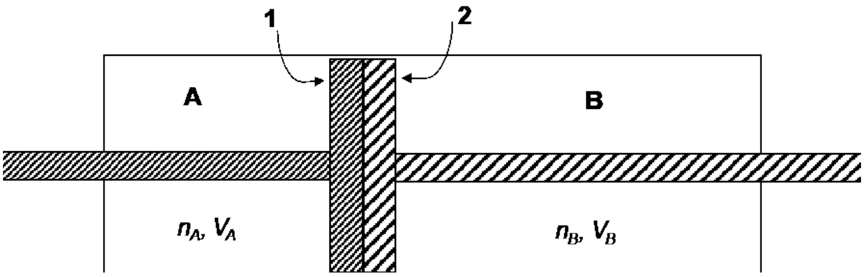
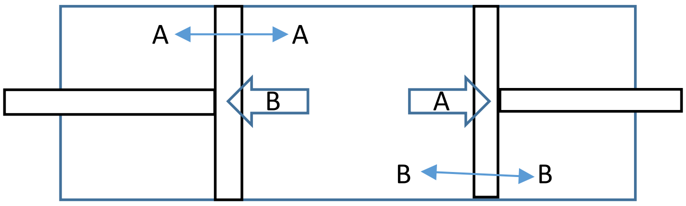
Homework 6 solutions

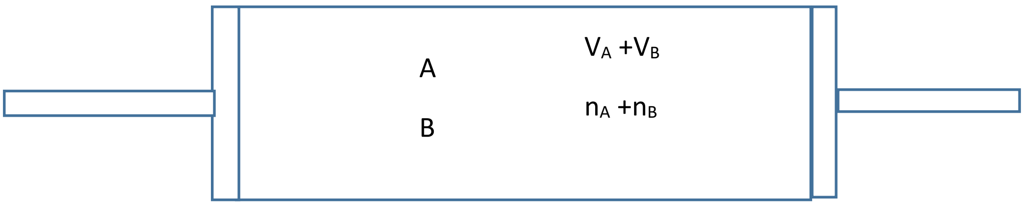
<u>Exercise 1.</u>

Derive the equation for the entropy of mixing ($\Delta_{mix}S = -R\sum n_i \ln x_i$) and the Gibbs free energy of mixing ($\Delta_{mix}G = RT\sum n_i \ln x_i$) as applied to two ideal gases only, by carrying out a reversible and isothermal mixing process in the apparatus shown below. Piston 1 is permeable only to gas A and piston 2 is permeable only to gas B. Initially, the two pistons are in contact, so that gas A is entirely in the left chamber and gas B is entirely to the right as shown, and the pressure in the two chambers is the same p_A=p_B=p. Finally, the two pistons are at the ends of the cylinder, thus gases have been mixed by passage through the pistons into the space between them.



The pressure on piston 1 by gas A is the same on both sides. The pressure exerted by gas A on piston 2 causing its movement to the right. When this process is carried out reversibly and isothermally (such as placing the apparatus in contact with a heat reservoir at temperature *T*), the work performed by gas A is the expansion work from volume V_A to the final volume V_A+V_B:





$$W_A = -\int_{V_A}^{V_A+V_B} p_A dV = -\int_{V_A}^{V_A+V_B} \frac{n_A RT}{V} dV = -n_A RT \ln\frac{V_A+V_B}{V_A}$$

Likewise, the expansion work by gas B:

$$W_B = -\int_{V_B}^{V_A+V_B} p_B dV = -\int_{V_B}^{V_A+V_B} \frac{n_B RT}{V} dV = -n_B RT \ln\frac{V_A+V_B}{V_B}$$

Because the internal energy of the ideal gas is unchanged, according to the first law, the total heat transfer must be equal to the total work of the two gases:

$$Q = -(W_A + W_B)$$

The entropy change:

$$\Delta_{mix}S \int \frac{\delta q}{T} = \frac{Q}{T}$$

Or

$$\Delta_{mix}S = \left(n_A R \ln \frac{V_A + V_B}{V_A} + n_B R \ln \frac{V_A + V_B}{V_B}\right)$$

$$\Delta_{mix}S = -\left(n_A R \ln \frac{V_A}{V_A + V_B} + n_B R \ln \frac{V_B}{V_A + V_B}\right)$$

Initially, $p_a = p_b = p$ and therefore:

$$\frac{V_A}{V_A + V_B} = \frac{n_A RT/\mathrm{p}}{(n_A + n_B)RT/p} = \frac{n_A}{n_A + n_B} = x_A$$

Similar expression for x_B, therefore:

$$\Delta_{mix}S = -R(n_A \ln x_A + n_B \ln x_B)$$

To derive $\Delta_{mix}G$, we also have to know $\Delta_{mix}H$

$$H = U + pV = U + nRT$$

Before mixing

$$H_A = U_A + n_A RT \qquad H_B = U_B + n_B RT$$

After mixing

$$H_{A+B} = U_{A+B} + (n_A + n_B)RT$$

$$\Delta_{mix}H = H_{A+B} - (H_A + H_B) = U_{A+B} - (U_A + U_B) = 0$$

Since the internal energy is only as a function of temperature, the enthalpy of mixing of ideal gases is zero under isothermal condition.

Therefore,

$$\Delta_{mix}G = \Delta_{mix}H - T\Delta_{mix}S = 0 - T\Delta_{mix}S = -RT(n_A \ln x_A + n_B \ln x_B)$$

Exercise 2.

You are responsible for the purchase of a gas cylinder which, before use, is stored at pressure of 200 atm and temperature 300 K in a cylindrical vessel of diameter $d = 0.2$ m and height $h = 2$ m. Would you prefer the gas behaved as an ideal gas or a real gas obeying the Van der Waals equation of state? For oxygen, the van der Waals constants are $a = 1.36 \frac{\text{atm liter}^2}{\text{mol}^2}$ and $b = 0.0318 \frac{\text{liter}}{\text{mol}}$). Hint – how much gas can be stored in each case?

The volume of the gas cylinder is

$$\pi \cdot \left(\frac{d}{2}\right)^2 \cdot h = 62.8 \text{ liter}$$

The gas constant is

$$R = 0.0821 \frac{\text{liter} \cdot \text{atm}}{\text{mol} \cdot \text{K}}$$

For an ideal gas, we have

$$n_{ideal} = pV/RT$$

Plugging in the numbers for an ideal gas

$$n_{ideal} = \frac{200[\text{atm}] * 62.8[\text{liter}]}{0.0821 \left[\frac{\text{liter} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right] * 300[\text{K}]} = 510 \text{ mol}$$

Plugging in the number for a van der Waals gas

$$\left(P + \frac{n_{vdw}^2 a}{V^2}\right) * (V - n_{vdw} b) = n_{vdw} RT$$

$$\left(200[\text{atm}] + \frac{(n_{vdw}[\text{mol}])^2 \cdot 1.36 \left[\frac{\text{atm} \cdot \text{liter}^2}{\text{mol}^2}\right]}{(62.8[\text{liter}])^2}\right) * \left(62.8[\text{liter}] - n_{vdw}[\text{mol}] \cdot 0.0318 \left[\frac{\text{liter}}{\text{mol}}\right]\right)$$

$$= n_{vdw}[\text{mol}] \cdot 0.0821 \left[\frac{\text{liter} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right] \cdot 300[\text{K}]$$

This is a cubic equation in n_{vdw} which has only one real solution, namely

$$n_{vdw} = 564 \text{ mol}$$

Conclusion: you would buy a larger quantity of gas if it behaved as a real gas.

Important note 1: If we are using units of [atm] for the pressure and [liter] for the volume, the gas constant should be $R = 0.082057 \left[\frac{\text{liter} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right]$

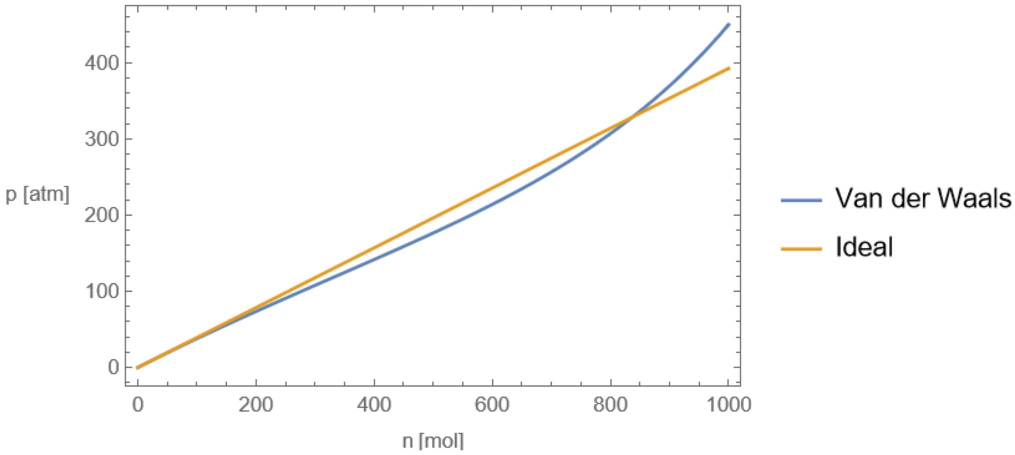
If $R = 8.314 \left[\frac{\text{J}}{\text{K} \cdot \text{mol}}\right]$, is used, then $b = 0.0318 \cdot 10^3 \left[\frac{\text{m}^3}{\text{mol}}\right]$ and $a = 1.36 \cdot (0.101325) \left[\frac{\text{J} \cdot \text{m}^3}{\text{mol}}\right]$.

Important note 2: It is a good idea to solve this problem graphically by expressing the pressure as a function of the number of moles of the gas. For the Van der Waals equation, we have:

$$p = \frac{nRT}{V - nb} - a\frac{n^2}{V^2}$$

And for ideal gas, we have:

$$p = \frac{nRT}{V}$$



Exercise 3.

One hundred moles of hydrogen gas at 298 K are reversibly and isothermally compressed from 30 to 10 litres. Let's explore this process with three different approximations: Van der Waals, Virial and ideal gas case.

The Van der Waals constants for hydrogen are

$$a = 0.2461 \frac{\text{atm liter}^2}{\text{mol}^2} \text{ and } b = 0.02668 \frac{\text{liter}}{\text{mol}}.$$

In the range of pressures from 0 to 1500 atm, the virial equation for hydrogen is

$$pv = RT(1 + Bp)$$

where $B = 6.4 * 10^{-4} \left(\frac{1}{atm}\right)$

Calculate the work that must be done on the system to produce the required change in the volume by assuming (a) that hydrogen is described by the Virial equation of state, (b) that hydrogen is behaving like a Van der Waals gas and (c) that hydrogen is assumed to behave as an ideal gas. Compare the different results.

a.

$$p_{Virial} = \frac{nRT}{V - BnRT}$$

$$W_{Virial} = -\int_{30}^{10} p_{Virial} dV = -\int_{30}^{10} \frac{nRT}{V - BnRT} dV = -nRT \ln\left(\frac{10 - BnRT}{30 - BnRT}\right)$$
$$= -100 \cdot 0.082 \cdot 298 \cdot \ln\left(\frac{10 - 6.4 \cdot 10^{-4} \cdot 100 \cdot 0.082 \cdot 298}{30 - 6.4 \cdot 10^{-4} \cdot 100 \cdot 0.082 \cdot 298}\right)$$
$$= 2969 \text{ [liter} \cdot \text{atm]} = 300.9 \text{ [kJ]}$$

b.

$$p_{vdw} = \frac{nRT}{V - nb} - \frac{n^2}{V^2} a$$

$$W_{vdw} = -\int_{30}^{10} p_{vdw} dV = -\int_{30}^{10} \left[\frac{nRT}{V - nb} - a\frac{n^2}{V^2}\right] dV = -nRT \ln\left(\frac{10 - nb}{30 - nb}\right) - an^2\left(\frac{1}{10} - \frac{1}{30}\right)$$
$$= -100 \cdot 0.082 \cdot 298 \cdot \ln\left(\frac{10 - 100 \cdot 0.02668}{30 - 100 \cdot 0.02668}\right) - 0.2461 \cdot 100^2 \cdot \left(\frac{1}{10} - \frac{1}{30}\right)$$
$$= 3051 \text{ [liter} \cdot \text{atm]} = 309.2 \text{ [kJ]}$$

c.

$$p_{ideal} = \frac{nRT}{V}$$

$$W_{ideal} = -\int_{30}^{10} p_{ideal} dV = -\int_{30}^{10} \frac{nRT}{V} dV = -nRT \ln\left(\frac{10}{30}\right)$$

$$= -100 \cdot 0.082 \cdot 298 \cdot \ln\left(\frac{10}{30}\right)$$

$$= 2685[\text{liter} \cdot \text{atm}] = 272.0\ [\text{kJ}]$$

Therefore, we have $W_{vdw} > W_{Virial} > W_{ideal}$