Solution for P5-24 | 10.213

Come up with an expression for the enthalpy and entropy departure functions for a gas that follows the Redlich-Kwong equation of state.

A. Entropy departure function

This problem is similar to Example 5.6 in Koretsky.

The Redlich-Kwong equation of state:

$$P = \frac{RT}{v-b} - \frac{a}{T^{1/2}v(v+b)}$$

As the Redlich-Kwong equation is explicit in pressure, it is convenient to choose T and v as the independent variables. Thus infinite volume is used as the limit of a ideal gas.

$$\Delta h^{dep}_{T,v} = h_{T,v} - h^{ideal}_{T,P} = (h_{T,v} - h^{ideal}_{T,v=\infty}) - (h^{ideal}_{T,P} - h^{ideal}_{T,v=\infty})$$

For an ideal gas, enthalpy is only a function of temperature. Thus

$$\Delta h^{dep}_{T,v} = h_{T,v} - h^{ideal}_{T,v=\infty}$$

$$\Delta h^{dep}_{T,v} = \int_{v=\infty}^{v} \left(\frac{\partial h}{\partial v}\right)_T dv \tag{1}$$

(1 point)

To find $\left(\frac{\partial h}{\partial v}\right)_T$, use the Equation 5.7 and Equation 5.18,

$$\left(\frac{\partial h}{\partial v}\right)_T = \left(\frac{T\,\partial s + v\,\partial P}{\partial v}\right)_T = T\left(\frac{\partial s}{\partial v}\right)_T + v\left(\frac{\partial P}{\partial v}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_v + v\left(\frac{\partial P}{\partial v}\right)_T \tag{2}$$

(1 point)

To find $\left(\frac{\partial P}{\partial T}\right)_v$ and $\left(\frac{\partial P}{\partial v}\right)_T$, integrate the RK EOS,

$$\left(\frac{\partial P}{\partial T}\right)_v = \frac{R}{v-b} + \frac{a}{2T^{3/2}v(v+b)}$$ (1 point)

$$\left(\frac{\partial P}{\partial v}\right)_T = -\frac{RT}{(v-b)^2} + \frac{a(2v+b)}{T^{1/2}v^2(v+b)^2} \qquad \text{(1 point)}$$

Substitute expressions for $\left(\frac{\partial P}{\partial T}\right)_v$ and $\left(\frac{\partial P}{\partial v}\right)_T$ into (2) and simplify

$$\left(\frac{\partial h}{\partial v}\right)_T = \frac{RT}{v-b} + \frac{aT}{2T^{3/2}v(v+b)} - \frac{RTv}{(v-b)^2} + \frac{av(2v+b)}{T^{1/2}v^2(v+b)^2}$$

$$\left(\frac{\partial h}{\partial v}\right)_T = \frac{-RTb}{(v-b)^2} + \frac{5a}{2T^{1/2}(v+b)^2} + \frac{3ab}{2T^{1/2}v(v+b)^2}$$

Substitute the above expression into Equation (1).

$$\Delta h^{dep}_{T,v} = \int_{v=\infty}^{v} \left[\frac{-RTb}{(v-b)^2} + \frac{5a}{2T^{1/2}(v+b)^2} + \frac{3ab}{2T^{1/2}v(v+b)^2}\right] dv \qquad \text{(1 point)}$$

Integrate the above expression using Mathematica or MATLAB.

$$\Delta h^{dep}_{T,v} = \frac{RTb}{v-b} - \frac{5a}{2T^{1/2}(v+b)} + \frac{3a\left(b+(b+v)\left(\ln v - \ln(v+b)\right)\right)}{2bT^{1/2}(v+b)} \qquad \text{(1/2 point)}$$

Solution for P5-24

10.213

B. Entropy departure function

$$\Delta s_{T,v}^{dep} = s_{T,v} - s_{T,v^{ideal}}^{ideal} = (s_{T,v} - s_{T,v=\infty}^{ideal}) - (s_{T,v^{ideal}}^{ideal} - s_{T,v=\infty}^{ideal})$$

Note that v^{ideal} is the volume of the gas at ideal condition. It is not equal to v.

$$\Delta s_{T,v}^{dep} = \int_{v=\infty}^{v} \left(\frac{\partial s}{\partial v}\right)_T dv - \int_{v=\infty}^{v^{ideal}} \left(\frac{\partial s}{\partial v}\right)_T dv \qquad (3)$$

(1 point)

Using Maxwell Relations Equation 5.18

$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v$$

Thus Equation (3) becomes

$$\Delta s_{T,v}^{dep} = \int_{v=\infty}^{v} \left(\frac{\partial P}{\partial T}\right)_v dv - \int_{v=\infty}^{v^{ideal}} \left(\frac{\partial P}{\partial T}\right)_v^{ideal} dv \qquad (4)$$

(1 point)

From earlier part, $\left(\frac{\partial P}{\partial T}\right)_v$ for real gas:

$$\left(\frac{\partial P}{\partial T}\right)_v = \frac{R}{v-b} + \frac{a}{2T^{3/2}v(v+b)}$$

For an ideal gas,

$$\left(\frac{\partial P}{\partial T}\right)_v^{ideal} = \frac{R}{v}$$

Substitute the above expressions into Equation (4) and integrate

$$\Delta s_{T,v}^{dep} = \int_{v=\infty}^{v} \left[\frac{R}{v-b} + \frac{a}{2T^{3/2}v(v+b)}\right] dv - \int_{v=\infty}^{v^{ideal}} \frac{R}{v} dv \qquad \text{(1 point)}$$

Solution for P5-24 | **10.213**

To eliminate the problem of singularity in the second integral, add and subtract ${}_{v=}^{v}\ \frac{R}{v}dv$

$$\Delta s_{T,v}^{dep} = {}_{v=}^{v}\ \frac{R}{v-b} + \frac{a}{2T^{3/2}v(v+b)} - \frac{R}{v}dv - {}_{v}^{v^{ideal}}\ \frac{R}{v}dv \qquad \text{(1 point)}$$

$$\Delta s_{T,v}^{dep} = R\left[\ln(v-b) - \ln v\right] + \frac{a(\ln v - \ln(v+b))}{2bT^{3/2}} - R\ln\frac{v^{ideal}}{v} \qquad \text{(1/2 point)}$$

Note on the infinity limit:

$$\Delta s_{T,v}^{dep} = {}_{v=}^{v}\ \frac{P}{T}\ {}_{v}\ dv - {}_{v=}^{v^{ideal}}\ \frac{P}{T}\ {}_{v}^{ideal}\ dv$$

$$= {}_{v=}^{v}\ \frac{P}{T}\ {}_{v}\ dv - {}_{v=}^{v^{ideal}}\ \frac{R}{V}dv$$

To eliminate the problem of singularity in the second integral, add and subtract ${}_{v=}^{v}\ \frac{R}{v}dv$

$$\Delta s_{T,v}^{dep} = {}_{v=}^{v}\ \frac{P}{T}\ {}_{v}\ - \frac{R}{V}dv - {}_{v}^{v^{ideal}}\ \frac{R}{V}dv$$

You can combine the two terms in the first integral

$$\Delta s_{T,v}^{dep} = {}_{v=}^{v}\ \frac{}{T}\ P - \frac{RT}{V}\ dv - {}_{v}^{v^{ideal}}\ \frac{R}{V}dv$$

At the limit of v→∞, $P \quad \frac{RT}{V}$. Thus the integral goes to zero at limit of v→∞.

This is why the first integral can have infinity as a limit but not the second integral.