Exercise 5

Problem 1:

a. Show the residual function of molar Helmholtz energy ($a^{R,P}$) as integral with respect to volume
b. Evaluate the residual property for residual molar Helmholtz energy ($a^{R,P}$) as integral with respect to volume using 2nd virial EOS

a) From the lectures: The residual function for an energy e with respect to volume is:

$$e^{R,P}_{(T,P)} = \int_{\infty}^{V}\left[\left(\frac{\partial e}{\partial V}\right)_T - \left(\frac{\partial e}{\partial V}\right)_T^{idg}\right] dV + \int_{V^{idg}}^{V}\left(\frac{\partial e}{\partial V}\right)_T dV$$

This gives that:

$$a^{R,P}(T,P) = \int_{\infty}^{V}\left[\left(\frac{\partial a}{\partial V}\right)_t - \left(\frac{\partial a}{\partial V}\right)_T^{idg}\right] dV + \int_{V^{idg}}^{V}\left(\frac{\partial a}{\partial V}\right)_T dV$$

Total differential of A:

$$dA = \left(\frac{\partial A}{\partial V}\right)_T dv + \left(\frac{\partial A}{\partial T}\right)_V dT$$

Combining 1st and 2nd law

$$dA = -pdV - SdT$$

$$\Rightarrow \left(\frac{\partial A}{\partial V}\right)_T = -p, \left(\frac{\partial A}{\partial T}\right)_V = -S$$

$$\Rightarrow a^{R,P}(T,V) = \int_{\infty}^{V}(-p + p^{ig})\, dV + \int_{V^{ig}}^{V}(-p^{ig})\, dV$$

For p^{ig}: Ideal gas law $p^{ig} = \frac{RT}{V}$

$$\Rightarrow a^{R,P}(T,V) = \int_{\infty}^{V}\left(\frac{RT}{V} - p\right) dV + \int_{V^{ig}}^{V} -\frac{RT}{V}\, dV$$

$$= \int_{\infty}^{V}\left(\frac{RT}{V} - p\right) dV - RT \ln\frac{V}{V^{ig}}$$

Compressibility factor $Z = \frac{pV}{RT}$

For ideal gas: $Z^{ig} = \frac{pV^{ig}}{RT} = 1$, divide by Z^{ig} on both sides:

$$\Rightarrow Z = \frac{\cancel{p}V}{\cancel{RT}} \cdot \frac{\cancel{RT}}{\cancel{p} \cdot V^{ig}} = \frac{V}{V^{ig}}$$

$$\boxed{a^{R,P}(T,V) = \int_{\infty}^{V} \left(\frac{RT}{V} - p\right) dV - RT \ln Z}$$

b) Need to get an expression for p

2nd virial EOS: $Z = 1 + \frac{BP}{RT}$

Also $Z = \frac{PV}{RT}$

$$\Rightarrow \frac{PV}{RT} = 1 + \frac{BP}{RT}$$

$$P\left(\frac{V}{RT} - \frac{B}{RT}\right) = 1$$

$$P \cdot \frac{V-B}{RT} = 1$$

$$P = \frac{RT}{V-b}$$

$$\Rightarrow a^{R,P}(T,V) = \int_{\infty}^{V} \left(\frac{RT}{V} - p\right) dV - RT \ln Z$$

$$a^{R,P}(T,V) = \int_{\infty}^{V} \left(\frac{RT}{V} - \frac{RT}{V-B}\right) dV - RT \ln Z$$

$$= RT \Big[\ln V - \ln(V-B)\Big]_{\infty}^{V} - RT \ln Z$$

$$= RT \left[\ln \frac{V}{V-B}\right]_{\infty}^{V} - RT \ln Z \quad , \quad V \to \infty, \ln \frac{V}{V-B} = \ln 1 = 0$$

$$= RT \ln \frac{V}{V-B} - RT \ln Z$$

$$\boxed{\text{From } Z = \frac{pV}{RT} \Rightarrow V = \frac{ZRT}{p}}$$

$$= RT \ln\left(\frac{\frac{ZRT}{p}}{\underbrace{\frac{ZRT}{p} - B}_{}}\right) - RT \ln Z$$

multiply by $\frac{p}{RT}$ over and under
the fraction bar

$$= RT \ln\left(\frac{Z}{Z - \frac{BP}{RT}}\right) - RT \ln Z$$

$$\boxed{\begin{aligned} &\text{2nd virial EOS: } Z = 1 + \frac{BP}{RT} \\ &\qquad \Rightarrow Z - \frac{BP}{RT} = 1 \end{aligned}}$$

$$= RT \ln Z - RT \ln Z = 0$$

$$\boxed{a^{R,P}(T,V) = 0}$$

Problem 2:

Derive relations for other residual properties by application of the generic relationships between thermodynamic functions on the residual part of the functions.

a. Find
   I. Residual entropy $s^{R,P}$ from residual helmholtz energy
   II. Residual internal energy $u^{R,P}$ from residual helmholtz and residual entropy or any other residual relationship

b. Show chemical potential from Gibbs residual property $g^{R,P}$ (T,P,n) and Helmholtz residual property $a^{R,P}$(T,V,n)

a) I: In 1 it was found that $\left(\frac{\partial A}{\partial T}\right)_V = -S$

It then follows that (using $Z = \frac{V}{V_{ig}}$ as the virial EOS is not mentioned)

$$s^{R,P} = \frac{\partial}{\partial T}\left(-a^{R,P}(T,V)\right)_V$$

$$= \frac{\partial}{\partial T}\left(-\int_{\infty}^{V}\left(\frac{RT}{V} - p\right)dV + RT \ln \frac{V}{V_{ig}}\right)_V$$

$$s^{R,P} = \frac{\partial}{\partial T}\left(\int_{\infty}^{V}\left(p - \frac{RT}{V}\right)dV\right)_V + R \ln \frac{V}{V_{ig}}$$

II: We know that $A = U - TS$

$\Rightarrow U = A + TS$

Which should mean that

$$u^{R,P} = a^{R,P} + T \cdot s^{R,P}$$

$$= \int_{\infty}^{V}\left(\frac{RT}{V} - p\right)dV - \cancel{RT \ln \frac{V}{V_{ig}}} + T \cdot \frac{\partial}{\partial T}\left(\int_{\infty}^{V}\left(p - \frac{RT}{V}\right)dV\right)_V + \cancel{RT \ln \frac{V}{V_{ig}}}$$

The integral is independent of T, and V is to be kept constant in the derivation

$$= \int_{\infty}^{V}\left(\frac{RT}{V} - p\right)dV + \int_{\infty}^{V} T\left(\frac{\partial p}{\partial T}\right)_V - \frac{RT}{V}\, dV$$

The integrals have the same limits

$$= \int_{\infty}^{V} \cancel{\frac{RT}{V}} - p + T\left(\frac{\partial p}{\partial T}\right)_V - \cancel{\frac{RT}{V}}\, dV$$

$$\boxed{u^{R,P} = \int_{\infty}^{V} T \cdot \left(\frac{\partial p}{\partial T}\right)_V - p\, dV}$$

b) We have that $G = H - TS$

$$\Rightarrow G^{R,P} = H - H^{ig} - T(S - S^{ig})$$

$$G^{R,P} = H^{R,P} - T \cdot S^{R,P}$$

For pressure, as $p \to 0$ we experience ideal behavior (in contrast to using V)

<u>$H^{R,P}$</u>

The total diff of H with regards to p, T:

$$dH = \left(\frac{\partial H}{\partial T}\right)_p \overset{0}{\cancel{dT}} + \left(\frac{\partial H}{\partial p}\right)_T dp$$

$$H^{R,P} = \int_0^p \left(\frac{\partial H}{\partial p}\right)_T - \left(\frac{\partial H}{\partial p}\right)_T^{ig} dp + \cancel{\int_{p^{ig}}^{p} \left(\frac{\partial H}{\partial p}\right)_T^{ig}}$$

as $p^{ig} = 0$, the correction term can

Expansion rule of $H(S,p)$

$$\left(\frac{dH}{\partial p}\right)_T = \left(\frac{\partial H}{\partial S}\right)_p \left(\frac{\partial S}{\partial p}\right)_T + \left(\frac{\partial H}{\partial p}\right)_S \overset{1}{\cancel{\left(\frac{\partial p}{\partial p}\right)_T}}$$

From combining 1st + 2nd law and total diff $\left(\frac{\partial H}{\partial S}\right)_p = T$, $\left(\frac{\partial H}{\partial p}\right)_S = V$

Maxwell relation: $\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p \Rightarrow \left(\frac{\partial H}{\partial p}\right)_T = V - T \cdot \left(\frac{\partial V}{\partial T}\right)_p$

$$H^{R,P} = \int_0^p V - T \cdot \left(\frac{\partial V}{\partial T}\right)_p - \left(V^{ig} - T \cdot \left(\frac{\partial V^{ig}}{\partial T}\right)_p\right) dp = \int_0^p V - T \cdot \left(\frac{\partial V}{\partial T}\right)_p - \cancel{\left(\frac{RT}{p} - T \cdot \frac{R}{p}\right)} dp = \int_0^p V - T \cdot \left(\frac{\partial V}{\partial T}\right)_p dp$$

<u>Using $S(T,p)$</u>

$$dS = \left(\frac{\partial S}{\partial T}\right)_p \overset{0}{\cancel{dT}} + \left(\frac{\partial S}{\partial p}\right)_T dp = -\left(\frac{\partial V}{\partial T}\right)_p dp$$

$$\Rightarrow S^{R,P} = \int_0^p -\left(\frac{\partial V}{\partial T}\right)_T + \left(\frac{\partial V}{\partial T}\right)_T^{ig} dp$$

$$= \int_0^p -\left(\frac{\partial V}{\partial T}\right)_T + \frac{R}{p} dp$$

Then $G^{R,P} = H^{R,P} - T \cdot S^{R,P}$

$$= \int_0^p V - T \cancel{\left(\frac{\partial V}{\partial T}\right)} dp - T \cdot \left(\int_0^p \frac{R}{p} - \cancel{\left(\frac{\partial V}{\partial T}\right)_T} dp\right)$$

$$= \int_0^p V - \frac{RT}{p} dp$$

(I see now that I have forgotten to use correct notation for molar basis)

import magic

$$g^{R,P} = \int_0^p \bar{V} - \frac{RT}{p} dp$$

Per def: $\mu_i = \left(\frac{\partial G}{\partial N_i}\right)_{T,P,N_{j\neq i}} = g_i$

$$\boxed{\mu_i^{R,P} = g_i^{R,P} = \int_0^P \bar{V} - \frac{RT}{P}\, dp}$$

From helmholtz:

Different def: $\mu_i = \left(\frac{\partial A}{\partial N_i}\right)_{T,V,N_{i\neq j}}$

$$\Rightarrow \boxed{\mu_i^{R,P} \text{ “} = \text{” } a_i^{R,P} = \int_\infty^V \Big(\underset{\substack{\uparrow \\ \text{Constent} \\ \text{in derivation}}}{\frac{RT}{V}} - \overset{\substack{\text{not constent} \\ \downarrow}}{\left(\frac{\partial p}{\partial N_i}\right)_{T,V,N_{i\neq j}}} \Big) dV - RT \ln \underset{\substack{\uparrow \\ \text{constent} \\ \text{in derivation}}}{\frac{V}{V_{ig}}}}$$

Problem 3:

A gas has an ideal gas heat capacity of $C_P^* = (7/2)R$ and is described by the equation of state:

$$Z = 1 + \frac{CP^2}{RT}$$

With C = 100 cm³/bar.mol

a) Find a general expression for the residual molar enthalpy for this gas
b) Find a general expression for the residual molar entropy for this gas
c) Find ΔH and ΔS for the gas if it is isothermally compressed from P = 1 bar and T = 400K to P = 50 bar and T = 400 K.

a) In problem 2, it was found that

$$h^{R,P} = \int_0^P \bar{V} - T\left(\frac{\partial \bar{V}}{\partial T}\right)_p dp \quad , \quad \text{using that } Z = \frac{p\bar{V}}{RT} = 1 + \frac{Cp^2}{RT} \Rightarrow \bar{V} = \frac{RT}{p} + Cp$$

$$= \int_0^P \cancel{\frac{RT}{p}} + Cp - \cancel{T\frac{R}{p}}\ dp$$

$$= \frac{Cp^2}{2}$$

$$\boxed{h^{R,P} = \frac{Cp^2}{2}}$$

b) It was found in problem 2 that:

$$s^{R,P} = \int_0^P -\left(\frac{\partial \bar{V}}{\partial T}\right)_T + \frac{R}{p}\, dp$$

$$= \int_0^P -\frac{R}{p} + \frac{R}{p}\, dp = 0$$

$$\boxed{s^{R,P} = 0}$$

c) $\Delta h = h_2 - h_1 = (h_2 - h_2^{ig}) - (h_1 - h_1^{ig}) + (h_2^{ig} - h_1^{ig})$

$= h_2^R - h_1^R + \Delta h^{ig}$

Previous exercises: $dH = C_p\, dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_p\right] dp$

Isothermal process: $dT = 0$

Ideal gas: $V = \frac{RT}{P}$, $T \cdot \left(\frac{\partial V}{\partial T}\right)_p = T \cdot \frac{R}{P} \Rightarrow dH = 0 \Rightarrow \Delta h^{ig} = 0$

$$\Delta h = h_2^R - h_1^R = \frac{C}{2}\left(p_2^2 - p_1^2\right) = \frac{100\ \text{cm}^3/\text{bar}\cdot\text{mol}}{2}\left((50\ \text{bar})^2 - (1\ \text{bar})^2\right) = 124950\ \frac{\text{cm}^3 \cdot \text{bar}}{\text{mol}}$$

$$\left[\frac{10^5\ \cancel{\text{Pa}}}{1\ \text{bar}} \cdot \frac{1\ \text{J}/\cancel{\text{m}^3}}{\cancel{\text{Pa}}} \cdot \frac{10^{-6}\ \cancel{\text{m}^3}}{\text{cm}3} \Rightarrow 1\ \text{cm}^3\ \text{bar} = 10^{-1}\ \frac{\text{J}}{\text{bar}\cdot\text{cm}^3}\right]$$

$\Delta h = 12495\ \text{J/mol}$

$$\boxed{\Delta h = 12{,}495\ \text{kJ/mol}}$$

$\Delta S = S_2 - S_1 = (S_2 - S_2^{ig}) - (S_1 - S_1^{ig}) + (S_2^{ig} - S_1^{ig})$

$= S_2^R - S_1^R + \Delta S^{ig}$

From previous exercises $dS = \frac{C_p}{T} \cancelto{0}{dT} - \left(\frac{\partial V}{\partial T}\right)_p dp$

For ideal gas $\left(\frac{\partial V}{\partial T}\right)_p = \frac{R}{P}$

$$\Rightarrow \Delta S^{ig} = \int_{P_1}^{P_2} -\frac{R}{P}\, dp = R \ln\left(\frac{P_1}{P_2}\right) = 8{,}314\ \text{J/mol}\cdot\text{K} \cdot \ln\left(\frac{1\ \text{bar}}{50\ \text{bar}}\right)$$

$\Delta S^{ig} = -32{,}52\ \text{J/mol}\cdot\text{K}$

$$\boxed{\Delta S = S_2^R - S_1^R + \Delta S^{ig} = \Delta S^{ig} = -32{,}52\ \text{J/mol}\cdot\text{K}}$$

Problem 4:

A gas flows through an adiabatic nozzle at a steady state, entering at P = 5 bar and T = 400 °C and leaving at P = 1 bar. Assuming the nozzle is reversible, what is the temperature of the exiting gas? Assume the gas has an ideal gas heat capacity of $C_P^* = 40$ J/mol · K and follows the equation of state:

$$\underline{V} = \frac{RT}{P} - aTP$$

Where a = 1.00 cm³/mol.bar.K. Apply residual functions for entropy to solve the problem.

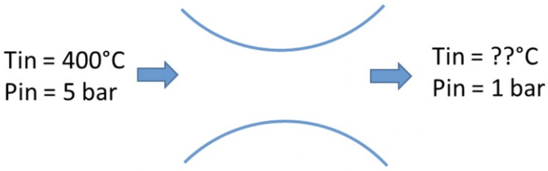

Figure 1: A schematic of nozzle for Problem 4

Process: $T_{in} = 400°C$, $P_{in} = 5$ bar $\xrightarrow[\text{reversible}]{}$ $T_{out} = ?$, $P_{out} = 1$ bar

For reversible processes: $\Delta S = 0$

$$S_2 - S_1 = 0$$

$$(S_2 - S_2^{ig}) - (S_1 - S_1^{ig}) + (S_2^{ig} - S_1^{ig}) = 0$$

$$S_2^{R,P} - S_1^{R,P} + \Delta S^{ig} = 0$$

I realize that you probably want an energy balance or something to argument for this being the case, but I'm currently down with covid, so my head is not capable of doing that at the moment. I was not able to come to the exercise hour either, so I used the formula straight from the book.

Seen in previous exercises, $S(T,p)$: $dS^{ig} = \frac{C_p^{ig}}{T}\,dT - \frac{R}{p}\,dp$ / integrating

$$\Delta S^{ig} = C_p^{ig} \ln\left(\frac{T_2}{T_1}\right) - R \ln\left(\frac{P_2}{P_1}\right)$$

From problem 3: $s^{R,P} = \int_0^P -\left(\frac{\partial \bar{V}}{\partial T}\right)_T + \frac{R}{P}\,dp$ / $\left(\frac{\partial \bar{V}}{\partial T}\right)_T = \frac{R}{P} - ap$

$$s^{R,P} = \int_0^P ap\,dp$$

$$s^{R,P} = \frac{ap^2}{2}$$

Then: $\frac{a}{2}(P_2^2 - P_1^2) + C_p^{ig} \ln\left(\frac{T_2}{T_1}\right) - R \ln\left(\frac{P_2}{P_1}\right) = 0$ / $C_v^{ig} = C_p^{ig} - R$

$$\Rightarrow \ln\left(\frac{T_2}{T_1}\right) = \frac{1}{C_p^{ig}} \left[\frac{a}{2}(P_1^2 - P_2^2) + R \ln\left(\frac{P_2}{P_1}\right)\right]$$

$T_2 = T_1 \cdot \exp\left(\frac{1}{C_p^{ig}} \left[\frac{a}{2}(P_1^2 - P_2^2) + R \ln\left(\frac{P_2}{P_1}\right)\right]\right)$ / $T_1 = 400°C = 673K$

$$T_2 = 673K \cdot \exp\left(\frac{1}{40\,\cancel{J/K \cdot mol}}\left[\frac{1\,\cancel{cm^3}/\cancel{mol} \cdot \cancel{bar} \cdot \cancel{K}}{2}\left(5^2 - 1^2\right)\cancel{bar^2} \cdot 10^{-1}\frac{\cancel{J}}{\cancel{bar \cdot cm^3}} + 8{,}314\ \cancel{J/K \cdot mol}\ \ln\left(\frac{1\,\cancel{bar}}{5\,\cancel{bar}}\right)\right]\right)$$

$$T_2 = 496{,}3K$$

$$\underline{\underline{T_2 = 223{,}3^\circ C}}$$