Exercise 3

$\hat{U}$: Property is based on mass, e.g (kJ/kg)

$\underline{U}$: Property is based on molar, e.g (kJ/mole)

Problem 1:

We can develop formal relationships between thermodynamic variables by relating properties of thermodynamic variables e.g. (T, P, μ,...) to the theory of homogeneous functions called Euler theorem.

a. Explain and show the mathematical formulation of Euler's theorem for homogeneous function
b. Show the fundamental equation for internal energy U = U(S,V,n$_i$) in the Euler form/equation
c. Show the Gibbs-Duhem relation from the Euler equation of b.

a) Euler's theorem:

For a homogenous function $f(x_1, x_2, \dots x_n)$ of order k, the following applies:

$$f(\lambda x_1, \lambda x_2, \dots, \lambda x_n) = \lambda^k f(x_1, x_2, \dots, x_n)$$

where λ is an arbitrary scaling factor.

by defining $x_i' = \lambda x_i$, then:

$$\frac{d}{d\lambda}\left(f(x_1', x_2', \dots, x_n')\right) = \frac{d}{d\lambda}\left(\lambda^k f(x_1, x_2, \dots, x_n)\right)$$

$$\sum_{i=1}^{n} \frac{\partial f}{\partial x_i'} \cdot \frac{\partial x_i'}{\partial \lambda} = k \cdot \lambda^{k-1} f(x_1, x_2, \dots, x_n) \quad / \quad \frac{\partial x_i'}{\partial \lambda} = \frac{\partial (x_i \cdot \lambda)}{\partial \lambda} = x_i$$

$$\sum_{i=1}^{n} \frac{\partial f}{\partial (x_i \lambda)} \cdot x_i = k \cdot \lambda^{k-1} f(x_1, x_2, \dots, x_n) \quad (\text{Choosing } \lambda = 1$$

$$\boxed{k f(x_1, x_2, \dots, x_n) = \sum_{i=1}^{n} x_i \frac{\partial f}{\partial x_i}} \text{ Eulers theorem}$$

b) Assuming that U is a homogenous function:

$$U(\lambda S, \lambda V, \lambda n_i) = \lambda^k U(S, V, n_i) \qquad / \frac{d}{d\lambda}$$

$$\Rightarrow k \lambda^{k-1} U(S, V, n_i) = \left(\frac{\partial U}{\partial (\lambda S)}\right)_{V, n_i} \frac{\partial (\lambda S)}{\partial \lambda} + \left(\frac{\partial U}{\partial (\lambda V)}\right)_{S, n_i} \frac{\partial (\lambda V)}{\partial V} + \left(\frac{\partial U}{\partial (\lambda n_i)}\right)_{S, V} \cdot \frac{\partial (\lambda n_i)}{\partial \lambda}$$

$$= \left(\frac{\partial U}{\partial(\lambda S)}\right)_{V,n_j} \cdot S + \left(\frac{\partial U}{\partial(\lambda V)}\right)_{S,n_i} \cdot V + \left(\frac{\partial U}{\partial(\lambda n_i)}\right)_{S,V} n_i \quad / \text{Choosing } \lambda=1,\ k=1$$

$$U(S,V,n_i) = \underbrace{\left(\frac{\partial U}{\partial S}\right)_{V,n_j}}_{=\,T} \cdot S + \underbrace{\left(\frac{\partial U}{\partial V}\right)_{S,n_i}}_{=\,-p} \cdot V + \underbrace{\left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_{j\neq i}}}_{=\,\mu_i \text{ by definition}} n_i$$

Seen in exercise 2

For m komponents:

$$\boxed{U(S,V,n_1,n_2,\dots,n_m) = TS - pV + \sum_{i=1}^{m} \mu_i \cdot n_i}$$

c) Want to show Gibbs-duhem relation:

$$0 = -SdT + Vdp - \sum_i n_i d\mu_i$$

From b: $U = TS - pV + \sum_{i=1} \mu_i \cdot n_i$

$$dU = d(TS) - d(pV) + \sum_{i=1} d(\mu_i n_i)$$

$$dU = TdS + SdT - pdV - Vdp + \sum_{i=1}\left[\mu_i dn_i + n_i d\mu_i\right]$$

From energy and entropy balances for open systems:

$$dU = TdS - pdV + \sum_{i=1} \mu_i dn_i$$

$$\Rightarrow \cancel{dU} = \cancel{dU} + SdT - Vdp + \sum_{i=1} n_i d\mu_i$$

$$\Rightarrow 0 = SdT - Vdp + \sum_{i=1} n_i d\mu_i \quad / \cdot(-1)$$

$$\underline{\underline{0 = -SdT + Vdp - \sum_{i=1} n_i d\mu_i}}$$

▨

Problem 2:

In a steady state flow process, 1 mol/s of air at 600 K and 1 atm is continuously mixed with 2 mol/s of air at 450 K and 1 atm. The product stream is at 400 K and 1 atm. A schematic representation of the process is shown in Figure 1. Determine the rate of heat transfer and the rate of entropy generation for the process. Assume that air is an ideal gas with $C_P = (7/2)\,R$, that the surroundings are at 300 K, and that kinetic and potential energy changes are negligible.

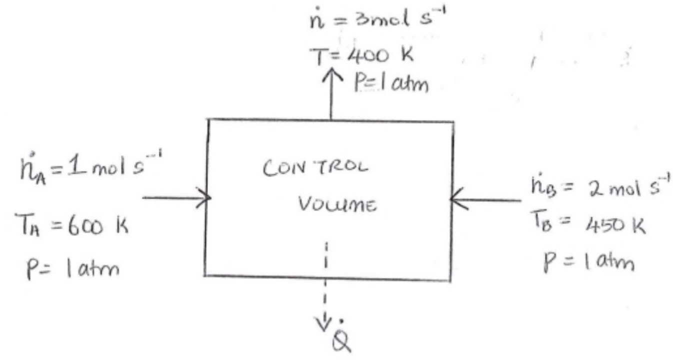

Figure 1: Process (control volume) described for Problem 2

- Want to find $\dot q$, and $\dot S_{gen}$
- Have: n, T, p and C_p (used in enthalpy expressions)
- Know: - Steady state => $\frac{dE}{dt} = 0$, $\dot n_{in} = \dot n_{out}$ (no reaction takes place)
  - $\Delta E_k, \Delta E_p \approx 0 \Rightarrow E \approx U$
  - Open system => Flow work, $H = U + PV$

The complete energy balance reduces to:

$$\sum_{i=A,B} H_i \dot n_i - H \cdot \dot n + \overset{\text{no shaft work}}{\cancel{\dot W_s}} + \underset{\text{the CV is constant}}{\cancel{\dot W_{E/C}}} + \dot q = 0$$

$$\Rightarrow H_A \cdot \dot n_A + H_B \cdot \dot n_B - H \cdot \dot n + \dot q = 0 \quad / \dot n = \dot n_A + \dot n_B$$

$$\dot q = \dot n_A \underbrace{(H - H_A)}_{\Delta H_A} + \dot n_B \underbrace{(H - H_B)}_{\Delta H_B}$$

From exercise 2: $dH = C_p dT \Rightarrow \Delta H = C_p \Delta T$

$$\dot q = \dot n_A C_p \Delta T_A + \dot n_B C_p \Delta T_B \quad / C_p = \tfrac{7}{2} R$$

$$\dot q = \tfrac{7}{2} \cdot 8{,}314\ \mathrm{J/}\cancel{\mathrm{mol}}\cdot\cancel{\mathrm{K}} \left(1\,\cancel{\mathrm{mol}}/\mathrm{s} \cdot (400\cancel{\mathrm{K}} - 600\cancel{\mathrm{K}}) + 2\,\cancel{\mathrm{mol}}/\mathrm{s} \cdot (400\cancel{\mathrm{K}} - 450\cancel{\mathrm{K}})\right)$$

$$\underline{\dot q = -8730\ \mathrm{J/s} = -8730\ \mathrm{W}}$$

Entropy balance:

$$\overset{0\ \text{steady state}}{\cancel{\frac{dS}{dt}}} = \dot S_{gen} + \sum_{in} \dot n_i S_i - \sum_{out} \dot n_i S_i + \underbrace{\dot S_{surr}}_{= \frac{\dot q}{T_{surr}}\ \text{(2nd law)}}$$

$$\dot S_{gen} = \sum_{out} \dot n_i S_i - \sum_{in} \dot n_i S_i - \frac{\dot q}{T_{surr}}$$

$$\dot S_{gen} = \dot n_A \Delta S_A + \dot n_B \Delta S_B - \frac{\dot q}{T_{surr}}$$

We have constant p, V

$$H = U + pV \Rightarrow dH = dU + pdV + \overset{dp=0}{\cancel{Vdp}}$$
$$= dq - \cancel{pdV} + \cancel{pdV}$$
$$= dq$$

$$dH = C_p dT \Rightarrow dq = C_p dT$$

$$dS = \frac{dq}{T} = C_p \frac{dT}{T} \Rightarrow \boxed{\Delta S = C_p \ln\left(\frac{T_2}{T_1}\right)}$$

$$\dot{S}_{gen} = \dot{n}_A \Delta S_A + \dot{n}_B \Delta S_B - \frac{\dot{q}}{T_{surr}}$$

$$= \frac{7}{2} R \left(\dot{n}_A \ln\left(\frac{400}{600}\right) + \dot{n}_B \ln\left(\frac{400}{450}\right)\right) - \frac{\dot{q}}{T_{surr}}$$

$$= \frac{7}{2} \cdot 8{,}314 \ \frac{J}{K \cdot \cancel{mol}} \left(1 \cancel{mol}/s \cdot \ln\left(\frac{2}{3}\right) + \underset{\uparrow \atop \cancel{mol}/s}{2} \ln\left(\frac{8}{9}\right)\right) - \frac{-8730 \ J/s}{300 \ K}$$

$$\underline{\underline{\dot{S}_{gen} = 10{,}45 \ W/K}}$$

Problem 3:

One mole of a gas is placed in a closed system with a 20 L vessel initially at T = 300 K. The vessel is then isothermally expanded to 40 L. The gas follows equation of state:

$$P = \frac{RT}{\underline{V}} + \frac{a}{\underline{V}^2}$$

where a = - 40 L^2 · atm/mol^2 and R = 0.08206 L · atm/mol · K.

a. Derive an expression relating $(d\underline{H}/d\underline{V})_T$ to measurable properties.
b. Find $\Delta\underline{H}$ for the gas in this process.

a)

From 1st and 2nd law: Gibbs relation for H: $dH = TdS + Vdp$

Total derivative $\Rightarrow$ $dH = \left(\frac{\partial H}{\partial S}\right)_p dS + \left(\frac{\partial H}{\partial p}\right)_S dp$

$\Rightarrow T = \left(\frac{\partial H}{\partial S}\right)_p \quad , \quad V = \left(\frac{\partial H}{\partial p}\right)_S$

Partial derivative of H with respect to V:

$$\left(\frac{\partial H}{\partial V}\right)_T = \underset{\underset{T}{\parallel}}{\left(\frac{\partial H}{\partial S}\right)_p} \cdot \left(\frac{\partial S}{\partial V}\right)_T + \underset{\underset{V}{\parallel}}{\left(\frac{\partial H}{\partial p}\right)_S} \cdot \left(\frac{\partial p}{\partial V}\right)_T$$

Maxwell relation: $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

Using the equation of state:

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{V}$$

$$\left(\frac{\partial p}{\partial V}\right)_T = -\frac{RT}{V^2} - \frac{2a}{V^3}$$

Combining:

$$\left(\frac{\partial H}{\partial V}\right)_T = \cancel{T\cdot\frac{R}{V}} + \cancel{V}\cdot\left(\cancel{-\frac{RT}{V^{\cancel{2}}}} - \frac{2a}{V^{\cancel{3}2}}\right)$$

$$\underline{\underline{\left(\frac{\partial H}{\partial V}\right)_T = -\frac{2a}{V^2}}}$$

b) As T is constant (isothermal expansion) we should obviously use the answer from a). N is constant => $dN = 0$. Using the EOS in the assignment, we can define two of (p, V, T) and the other will be defined. "Assuming" H is a function of V, T:

$$dH = \left(\frac{\partial H}{\partial V}\right)_T dV + \left(\frac{\partial H}{\partial T}\right)_V \overset{0 \text{ isothermal}}{\cancel{dT}}$$

$$dH = \left(\frac{\partial H}{\partial V}\right)_T dV = -\frac{2a}{V^2} \quad / \text{integrating}$$

$$\Delta H = \cancel{-}2a \cdot \left[\frac{1}{\cancel{-}1} \cdot \frac{1}{V}\right]_{20\,L}^{40\,L} = -2 \cdot 40\,L^{\cancel{2}} \cdot atm/mol^2 \cdot \left[\frac{1}{40\,\cancel{L}} - \frac{1}{20\,\cancel{L}}\right]$$

$$= -2 \cdot L \cdot atm/mol^2 + 4\,L \cdot atm/mol^2$$

$$= 2\,L \cdot atm/mol^2$$

For 1 mole:

$$\Delta H = 2\,L \cdot atm/mol$$

Want joule, Joule = $Pa \cdot m^3$

$$= 2\,\frac{\cancel{L} \cdot \cancel{atm}}{mol} \cdot \frac{1\,m^3}{1000\,\cancel{L}} \cdot \frac{1{,}01325 \cdot 10^5\,Pa}{1\,\cancel{atm}}$$

$$\Delta H = 202{,}65\,J/mol$$

I see that I "forgot" the molar notation "_", which i should have done. I will not change it now 😅 This is why I have "per mole" in my answer as well... So I will cancel it out "magically".

$$\underline{\underline{\Delta H = 202{,}65\,J}}$$

Problem 4:

5 moles of gas are confined in a piston-cylinder device (Figure 2). At the beginning of the process, the gas has T = 300 K and V = 100 L. If the gas is compressed isothermally to a final volume of 15 L, how much work is required, and how much heat is added or removed? Assume the heat capacity is constant at C_V = 30 J/mol . K and that the gas is modelled by the van der Waals equation of state

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

With a = 1.40 L²bar/mol² and b = 0.038 L/mol. Provide the answer in unit Joule (J).

$$dT = \Delta T = 0$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

Should start from, or get to U.

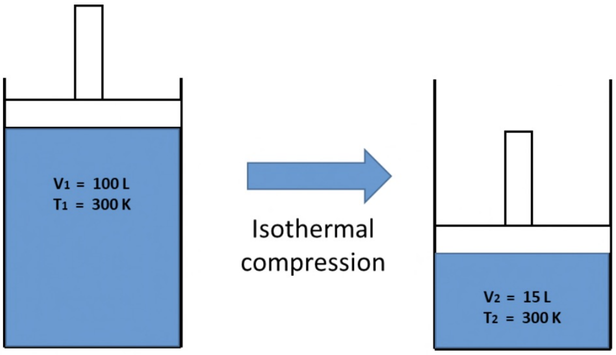

Figure 2: Isothermal compression of gas in piston cylinder device

Using the energy balance for a closed system (without shaft work)

I was asked in the exercise hours to show how I got this expression, the derivation is attached on the last page.

$$N \cdot \Delta \underline{U} = Q + W_{E/C} = Q + W_c$$, We have a compression

Calculating W_c from formulas given in the lectures:

$$W_c = -\int P dV = -\int_{100\,L}^{15\,L} \frac{RT}{V-b} - \frac{a}{V^2}\, dV$$

This time, remembering that $\underline{V} = \frac{V}{N} \Rightarrow V = N\underline{V}$

$$dV = N\,d\underline{V}$$

limits: $V = 100L \Rightarrow \underline{V} = 20 L/mol$

$V = 15\,L \Rightarrow \underline{V} = 3 L/mol$

(Not making the same mistake twice...)

$$W_c = -N \int_{20\,L/mol}^{3\,L/mol} \frac{RT}{\underline{V}-b} - \frac{a}{\underline{V}^2}\, d\underline{V}$$

$$= -N \left[\frac{RT}{1} \ln(\underline{V}-b) - \frac{a}{-1\underline{V}}\right]_{20\,L/mol}^{3\,L/mol}$$

$$= -N \left[RT \ln(\underline{V}-b) + \frac{a}{\underline{V}}\right]_{20}^{3}$$

$$= -5\,m\cancel{ol} \cdot \left[8{,}314\ J/\cancel{mol}\cdot\cancel{K} \cdot 300\cancel{K} \cdot \ln\left(\frac{3-0{,}038}{20-0{,}038}\right) + 1{,}40\,L^{\cancel{2}} \cdot bar/mo\cancel{l}^{\cancel{2}} \left(\frac{1}{3\cancel{L}/\cancel{mol}} - \frac{1}{20\cancel{L}/\cancel{mol}}\right) \cdot \frac{10^5 Pa \cdot 1m^3}{1\,bar \cdot 1000\,dm^3}\right]$$

$$\Rightarrow \underline{\underline{W_c = 23596\ J}}$$

The differential of U in useful variables:

$$\partial U = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V \overset{0,\ \text{isothermal}}{\cancel{dT}}$$

Using the same trick as in the last problem:

1st + 2nd law: $dU = TdS - pdV$

Total differential: $dU = \left(\frac{\partial U}{\partial S}\right)_V dS - \left(\frac{\partial U}{\partial V}\right)_S dV$

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

Partial derivative of U with respect to V at const T:

$$\left(\frac{\partial U}{\partial V}\right)_T = \underset{\overset{\shortparallel}{T}}{\left(\frac{\partial U}{\partial S}\right)_V} \underbrace{\left(\frac{\partial S}{\partial V}\right)_T}_{\text{Maxwells relation}} + \underset{\overset{\shortparallel}{-p}}{\left(\frac{\partial U}{\partial V}\right)_S} \overset{1}{\cancel{\left(\frac{\partial V}{\partial V}\right)_T}}$$

$$= \left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b}$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T \cdot \frac{R}{V-b} - p = \frac{RT}{V-b} - \frac{RT}{V-b} + \frac{a}{V^2} = \frac{a}{V^2}$$

I forgot the molar notation again... I fix it below

Which means that

$$d\underline{U} = \frac{a}{\underline{V}^2} d\underline{V}$$

$$\Delta\underline{U} = -a \cdot \left[\frac{1}{\underline{V}}\right]_{20\,\text{mol/L}}^{3\,\text{mol/L}}$$

$$\Delta\underline{U} = -1{,}40\ \frac{\cancel{L}^{\cancel{2}}\ \cancel{\text{bar}}}{\text{mol}^{\cancel{2}}} \left(\frac{1}{3\ \cancel{L}/\cancel{\text{mol}}} - \frac{1}{20\ \cancel{L}/\cancel{\text{mol}}}\right) \cdot \frac{10^5\ \text{Pa}}{1\ \cancel{\text{bar}}} \cdot \frac{1\ \text{m}^3}{10^3\ \cancel{L}}$$

$$\underline{\Delta\underline{U} = -40\ \text{J/mol}}$$

From the energy balance, then:

$$Q = N \cdot \Delta\underline{U} - W = 5\ \cancel{\text{mol}} \cdot \left(-40\ \text{J}/\cancel{\text{mol}} - 23596\ \text{J}\right) \Rightarrow \underline{\underline{Q = -23\ 796\ \text{J}}}$$

Derivation of energy balence for closed system

The complete energy balence

$$\frac{d}{dt}\left(M\left[\hat{U}+\frac{v^2}{2}+gh\right]\right)=\sum_{j=1}^{j=J}\left[\dot{m}_{j,in}\left(\hat{H}_j+\frac{v_j^2}{2}+gh_j\right)\right]-\sum_{k=1}^{k=K}\left[\dot{m}_{k,out}\left(\hat{H}_k+\frac{v_k^2}{2}+gh_k\right)\right]$$

$$+\dot{W}_S+\dot{W}_{E/C}+\dot{Q}$$

- Assuming that the changes in kinetic and potential energy are negligible compared to the change in internal energy $\frac{v^2}{2}\approx 0,\ gh\approx 0$
- The system is closed $\Rightarrow \dot{m}_{in}=\dot{m}_{out}=0$
- We have no shaft work $\Rightarrow \dot{W}_S=0$

The energy balence then reduces to:

$$\frac{d}{dt}M\hat{U}=\dot{W}_{E/C}+\dot{Q}$$

Using a molar and not a mass basis:

$$\frac{d}{dt}N\cdot\underline{U}=\dot{W}_{E/C}+\dot{Q}$$

Integration from before until after the compression

$$\boxed{N\Delta U=W_{E/C}+Q}$$