Exercise 4

Problem 1:

Make an overview of the Legendre transformations of internal energy U (H, A,G,O - the null potential) => Starting with the internal energy function in its canonical variables U(S,V,N) including all the relationships that can be derived based on the properties of the Legendre transformation (partial derivative of transformed function with respect to the original variable, partial derivative of transformed function with respect to the transformed variable, identities = independency of the order of derivation)

Legendre transform:

$$\varphi_i = f - \left(\frac{\partial f}{\partial x_i}\right)_{x_j,\dots,x_N} x_i$$

Where $\varphi_i(\xi_i, x_j, \dots x_N)$ is the transformed function,

$f(x_i, x_j, \dots, x_N)$ is the original function

and $\xi_i = \left(\frac{\partial f}{\partial x_i}\right)_{x_j,\dots,x_n}$ is the transformed variable

$$\Rightarrow \varphi_i = f - \xi_i x_i \quad (1)$$

Derivation of useful properties of the LT (needed in later calculations):

- The total differential of f: $df = \left(\frac{\partial f}{\partial x_i}\right)_{x_j,\dots,x_N} dx_i + \sum_{k\neq i}^{N} \left(\frac{\partial f}{\partial x_k}\right)_{\text{not } x_k} dx_k$

$$df = \xi_i \, dx_i + \sum_{k\neq i}^{N} \left(\frac{\partial f}{\partial x_k}\right)_{x_i, \text{not } x_k} dx_k \quad (2)$$

- The total differential of φ_i: $d\varphi_i = \left(\frac{\partial \varphi_i}{\partial f}\right)_{\xi_i, x_i} df + \left(\frac{\partial \varphi_i}{\partial \xi_i}\right)_{f, x_i} d\xi_i + \left(\frac{\partial \varphi_i}{\partial x_i}\right)_{f, \xi_i} dx_i$
  - ↳ using $\varphi_i(f, x_i, \xi_i)$

Using 1 : $= df - x_i \, d\xi_i - \xi_i \, dx_i$

Using 2 : $= \sum_{k\neq i}^{N} \left(\frac{\partial f}{\partial x_k}\right)_{x_i, \text{not } x_k} dx_k - x_i \, d\xi_i \quad (3)$

- The total differential of φ_i: $d\varphi_i = \left(\frac{\partial \varphi_i}{\partial \xi_i}\right)_{x_j,\dots,x_N} d\xi_i + \sum_{k\neq i}^{N} \left(\frac{\partial \varphi_i}{\partial x_k}\right)_{\xi_i, \text{not } x_k} dx_k \quad (4)$
  - ↳ using $\varphi_i(\xi_i, x_j, \dots, x_N)$
    - ↳ Allowed as φ_i is a function of f, which is a function of $x_i, \dots, x_N$

Combining 3 and 4 gives:

$$\left(\frac{\partial \varphi_i}{\partial \xi_i}\right)_{x_j,\dots,x_N} = -X_i \quad 5$$

$$\left(\frac{\partial \varphi_i}{\partial x_k}\right)_{\xi_i,\text{not } x_k} = \left(\frac{\partial f}{\partial x_k}\right)_{x_i,\text{not } x_k} = \xi_k \quad 6$$

by definition

- Repeated transform

$$\varphi_{ij} = \varphi_i - \xi_j X_j = f - \xi_i X_i - \xi_j X_j = f - \xi_j X_j - \xi_i X_i = \varphi_j - \xi_i X_i = \varphi_{ji}$$

$\Rightarrow \varphi_{ij} = \varphi_{ji}$

$\Rightarrow$ We "lose" a transformation per repeated LT.

- Using LT on $U(S,V,N)$:

- $A(T,V,N) = \varphi_1 \Rightarrow$ Use LT, $X_i = S$

$$\Rightarrow A = U - \left(\frac{\partial U}{\partial S}\right)_{V,N} \cdot S = U - \tau \cdot S$$

$A = U - TS$
$\tau = T$

$$\Rightarrow \boxed{\begin{aligned}\left(\frac{\partial U}{\partial S}\right)_{V,N} &= T \\ \left(\frac{\partial A}{\partial T}\right)_{V,N} &= -S\end{aligned}}$$

Using 5:

- $H(S,p,N) = \varphi_2 \Rightarrow$ Use LT with $X_i = V$

$$\Rightarrow H = U - \left(\frac{\partial U}{\partial V}\right)_{S,N} V = U - \pi V$$

$H = U + pV$
$\pi = -p$

$$\Rightarrow \boxed{\begin{aligned}\left(\frac{\partial U}{\partial V}\right)_{S,N} &= -p \\ \left(\frac{\partial H}{\partial p}\right)_{S,N} &= V\end{aligned}}$$

Using 5:

$(\pi = -p)$

- $G(T,p,N) = \varphi_{12} = U - \left(\frac{\partial U}{\partial S}\right)_{V,N} S - \left(\frac{\partial U}{\partial V}\right)_{S,N} V$

Using previous results: $= U - TS + pV$

Using 5: $$\boxed{\begin{aligned}\left(\frac{\partial G}{\partial T}\right)_{V,N} &= -S \\ \left(\frac{\partial G}{\partial p}\right)_{S,N} &= V \quad (\pi = -p)\end{aligned}}$$

- $O(T,p,\mu) = \varphi_{123} = U - \left(\frac{\partial U}{\partial S}\right)_{V,N} \cdot S - \left(\frac{\partial U}{\partial V}\right)_{S,N} V - \underbrace{\left(\frac{\partial U}{\partial N}\right)_{S,V}}_{= \mu \text{ by definition}} \cdot N$

$$= U - TS + pV - \mu N$$

$\Rightarrow$ $$\boxed{\begin{aligned}\left(\frac{\partial U}{\partial N}\right)_{S,V} &= \mu \\ \left(\frac{\partial O}{\partial T}\right)_{V,N} &= -S \\ \left(\frac{\partial O}{\partial p}\right)_{S,N} &= V \quad (p = -\pi) \\ \left(\frac{\partial O}{\partial \mu}\right)_{S,V} &= -N\end{aligned}}$$

From 5:

In addition:

$$O = U - TS + pV - \mu N$$

In exercise 3, assuming U to be an euler homogenous function:

$$U = TS - pV + \mu N$$

$$\Rightarrow O = U - U = 0 \quad \Rightarrow \quad \boxed{\begin{aligned}O &= 0 \\ U - TS + pV - \mu N &= 0\end{aligned}}$$

We can derive Gibbs-duhem from this

Problem 2:

Derive the relationships for calculation of TD properties of ideal gas (μ^{ig}; G^{ig}; A^{ig}; S^{ig}; U^{ig}) starting from Gibbs-Duhem Equation consider constant temperature and one component system

Gibbs-duhem eq:

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

Constant T, one component $\Rightarrow$ $dT=0$, $\sum_i n_i d\mu_i = N \cdot \mu$

$$\Rightarrow \quad Vdp - N \cdot \mu = 0 \quad (7)$$

• μ_{ig}

From 7 : $d\mu = \frac{V}{N} dp$, for ideal gas, $NRT = PV \Rightarrow V = \frac{NRT}{p}$ (8)

$$d\mu^{ig} = \frac{RT}{p} dp$$

$$\int_{\mu^{ig}(T,p^o)}^{\mu^{ig}(T,p)} d\mu^{ig} = RT \int_{p^o}^{p} \frac{dp}{p}$$

$$\Rightarrow \quad \mu^{ig}(T,p) = \mu^{ig}(T,p^o) + RT \ln\left(\frac{p}{p^o}\right)$$

$$\boxed{\mu^{ig}(T,p) = \mu_0^{ig}(T) + RT \ln\left(\frac{p}{p^o}\right)}$$

• G^{ig}

As $g^{ig} = \mu^{ig}$

molar gibbs   chemical potential

Then
$$\boxed{\begin{gathered} G^{ig} = N \cdot \mu^{ig} \\ G^{ig}(T,p,N) = N\left(\mu_0^{ig}(T) + RT \ln\left(\frac{p}{p^o}\right)\right) \end{gathered}}$$

• A^{ig}

- Euler's 1st theorem: $\sum x_i \left(\frac{\partial f}{\partial x_i}\right) = kf$
- $A(T,V,N)$, with $k=0$ for T, $k=1$ for V, $k=1$ for N

$$\Rightarrow A = \left(\frac{\partial A}{\partial V}\right)_{T,N} V + \left(\frac{\partial A}{\partial N}\right)_{T,V} N$$

Need $\left(\frac{\partial A}{\partial V}\right)_{T,N}$ and $\left(\frac{\partial A}{\partial N}\right)_{T,V}$. Using results from problem 1, and 6:

$$\left(\frac{\partial A}{\partial V}\right)_{T,N} = \left(\frac{\partial U}{\partial V}\right)_{S,N} = -p$$

$$\left(\frac{\partial A}{\partial N}\right)_{T,V} = \left(\frac{\partial U}{\partial N}\right)_{S,V} = \mu$$

$$\Rightarrow A = -pV + \mu N$$

Using 8 : $A^{ig} = -NRT + \mu^{ig} \cdot N$

$$\boxed{A^{ig} = -NRT + N \cdot \left[\mu_0^{ig}(T) + RT \ln\left(\frac{p}{p^\circ}\right)\right]}$$

or, $a^{ig} = \frac{A^{ig}}{N} \Rightarrow \boxed{a^{ig} = \mu_0(T) - RT\left(1 - \ln\frac{p}{p^\circ}\right)}$

• S^{ig}

In problem 1, it was found that: $-S = \left(\frac{\partial A}{\partial T}\right)_{V,N} \Rightarrow S = -\left(\frac{\partial A}{\partial T}\right)_{V,N}$

Performing the partial differentiation:

$$S = NR - N \cdot \left[\frac{\mu_0^{ig}(T)}{\partial T} + \frac{\partial}{\partial T}\left(RT \ln\left(\frac{p}{p^\circ}\right)\right)\right]$$

$$\frac{\partial}{\partial T}\left[RT \ln\left(\frac{p}{p^\circ}\right)\right] = R \ln\left(\frac{p}{p^\circ}\right) + RT \cdot \frac{\partial}{\partial T}\left(\ln\left(\frac{p}{p^\circ}\right)\right) = R \cdot \ln\left(\frac{p}{p^\circ}\right) + RT \cdot \frac{\partial \ln\left(\frac{p}{p^\circ}\right)}{d\left(\frac{p}{p_0}\right)} \frac{\partial}{\partial T}\left(\frac{p}{p^\circ}\right)$$

p is a function of T, p° is not, 8 $\Rightarrow = R \cdot \ln\left(\frac{p}{p^\circ}\right) + RT \frac{1}{\cancel{p/p^\circ}} \cdot \frac{1}{\cancel{p^\circ}} \cdot \frac{\partial}{\partial T}\left(\frac{NRT}{V}\right)$

$= R \cdot \ln\left(\frac{p}{p^\circ}\right) + RT \cdot \frac{1}{p} \cdot \frac{NR}{V} = R \ln\frac{p}{p^\circ} + R \cdot \frac{1}{p} \cdot \frac{NRT}{V}$ $\quad$ "= p"

$= R \cdot \ln\left(\frac{p}{p^\circ}\right) + R$

$$\Rightarrow S^{ig} = \cancel{NR} - N \cdot \left[\frac{\mu_0^{ig}(T)}{\partial T} + R \cdot \ln\left(\frac{p}{p^0}\right) + \cancel{R} \right]$$

$$\boxed{S^{ig} = -N \left[\frac{\mu_0^{ig}(T)}{\partial T} + R \cdot \ln\left(\frac{p}{p^0}\right) \right]}$$

- $\underline{U^{ig}}$

Using the definition of Helmholtz energy:

$$A = U - TS$$

$$\Rightarrow U = A + TS$$

$$U^{ig} = A^{ig} + TS^{ig}$$

$$= -NRT + N \cdot \left[\mu_0^{ig}(T) + \cancel{RT \ln\left(\frac{p}{p^0}\right)} \right] - T \cdot N \left[\frac{\mu_0^{ig}(T)}{\partial T} + \cancel{R \cdot \ln\left(\frac{p}{p^0}\right)} \right]$$

$$\boxed{U^{ig} = -NRT + N\mu_0^{ig}(T) - NT \frac{\mu_0^{ig}(T)}{\partial T}}$$

This can be shortened: (Not sure if this is necessary, but it was done in the lectures)

We have that $G(T, p^0, N) = \mu_0(T) \cdot N$

And also that

$$G(T, p^0, N) = H(T, p^0, N) - T \cdot S(T, p^0, N)$$

$$\Rightarrow \mu_0(T) \cdot N = H(T, p^0, N) - T \cdot S(T, p^0, N)$$

$$-S = \left(\frac{\partial G}{\partial T}\right)_{V,N} = N \frac{\partial \mu_0(T)}{\partial T}$$

Problem 1

$$\Rightarrow H_0^{ig} = N\left(\mu_0^{ig}(T) - T \cdot \frac{\partial \mu_0(T)}{\partial T}\right)$$

$$\boxed{U^{ig} = H_0^{ig} - NRT}$$

Problem 3:

Compare the obtained relationship for $U^{ig}(T)$ above with a relationships obtained by integration of the previously derived $dU^{ig}(T) = Cv\, dT$. (Apply Mayer's relation $Cp^{ig} - Cv^{ig} = NR$). How would you evaluate the $U^{o}(T^{o})$ and $H^{o}(T^{o})$? How is the standard reference state defined? How are reference data usually presented in the literature?

From problem 2: $U_{ig} = H_{ig} - NRT$ (The H°-notation was used for p° in the last problem, here: T°)

$$H_{ig} = N\left(\mu_0^{ig}(T) - T\frac{\partial \mu_0^{ig}(T)}{\partial T}\right)$$

Integrating dU^{ig}:

Mayer's relation

$$dU^{ig}(T) = C_V^{ig}\, dT = (C_p^{ig} - NR)\, dT$$ /Assume Cp to be a weak function of T

$$U^{ig}(T) - U_0^{ig} = (C_p^{ig} - NR)(T - T_0)$$

$$U^{ig} = U_0^{ig} + \underbrace{C_p^{ig}(T - T_0)}_{\Delta H^{ig} = H^{ig} - H_0^{ig}} - NR(T - T_0)$$

$$= U_0^{ig} + H^{ig} - H_0^{ig} - NRT - \underset{P_0V_0}{\underset{\parallel}{NRT_0}}$$

$$= \underbrace{U_0^{ig} - P_0V_0}_{= H_0^{ig} \text{ by definition of } H} + H^{ig} - H_0^{ig} - NRT$$

$$\underline{\underline{U^{ig} = H^{ig} - NRT}}$$ ⇒ Which is the same as problem 2

- I would calculate H° from: $H^{\circ}(T^{\circ}) = N\left(\mu_0^{ig}(T^{\circ}) - T^{\circ}\frac{\partial \mu_0^{ig}(T^{\circ})}{\partial T}\right)$

$$U_{ig}^{\circ}(T^{\circ}) = H_{ig}^{\circ}(T^{\circ}) - NRT^{\circ}$$

or, if I used a table, I would look it up.

- The standard reference state is defined differently depending on the most convenience in doing calculations for a system and differentically in different tables. Usually $T^{\circ} = 25°C$, $p^{\circ} = 1$ bar

- In tables the reference state is usually set to $U^{\circ} = 0$, and then other values is calculated in relation to U°.

Problem 4:

Derive an expression for each of the following that is, as much as possible, in terms of measurable properties: P, V, T, C_P, and C_V, and their partial derivatives with respect to each other. S can appear in the expression, but not derivatives of S. (Hint: Use manipulation of thermodynamic rules such as expansion rule, Maxwell's relation, triple product rule,...).

a. $(\partial H/\partial T)_V$
b. $(\partial H/\partial P)_T$
c. $(\partial U/\partial V)_P$
d. $(\partial A/\partial S)_P$

The expansion rule: $\left(\frac{\partial X}{\partial Y}\right)_Z = \left(\frac{\partial X}{\partial K}\right)_L \left(\frac{\partial K}{\partial Y}\right)_Z + \left(\frac{\partial X}{\partial L}\right)_K \left(\frac{\partial L}{\partial Y}\right)_Z$

a) In canonical variables: $H(S,p)$

Using the expansion rule:

$$\left(\frac{\partial H}{\partial T}\right)_V = \left(\frac{\partial H}{\partial S}\right)_p \left(\frac{\partial S}{\partial T}\right)_V + \left(\frac{\partial H}{\partial p}\right)_S \left(\frac{\partial p}{\partial T}\right)_V$$

In exercise 2, combining TD 1st and 2nd law:

$$dH = TdS + Vdp$$

Total differential:

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

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

We now have:

$$\left(\frac{\partial H}{\partial T}\right)_V = T \underbrace{\left(\frac{\partial S}{\partial T}\right)_V}_{\text{need to evaluate this}} + V \left(\frac{\partial p}{\partial T}\right)_V$$

For $S(T,V)$: $dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$

For $U(S,V)$: $dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$ / Problem 1: $\left(\frac{\partial U}{\partial S}\right)_V = T \, , \left(\frac{\partial U}{\partial V}\right)_S = -p$

Inserting dS into dU gives $dU(T,V)$:

$$dU = T\left[\left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV\right] - pdV = T\left(\frac{\partial S}{\partial T}\right)_V dT + \left[T\left(\frac{\partial S}{\partial V}\right)_T - p\right] dV$$

Total diff for $U(T,V)$: $dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$

We now see that $\left(\frac{\partial U}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V \underset{\text{per def}}{=} C_V$

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

$$\Rightarrow \boxed{\left(\frac{\partial H}{\partial T}\right)_V = C_V + V\left(\frac{\partial p}{\partial T}\right)_V}$$

b) $H(S,p)$

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

$$= T\left(\frac{\partial S}{\partial p}\right)_T + V$$

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

$$\boxed{\left(\frac{\partial H}{\partial p}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_p}$$

c) $$\left(\frac{\partial U}{\partial V}\right)_p = \left(\frac{\partial U}{\partial S}\right)_V \left(\frac{\partial S}{\partial V}\right)_p + \left(\frac{\partial U}{\partial V}\right)_S \cancelto{1}{\left(\frac{\partial V}{\partial V}\right)_p}$$

Need $\left(\frac{\partial S}{\partial V}\right)_p$

Using that $\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_z}$

$$\left(\frac{\partial S}{\partial V}\right)_p = \frac{1}{\left(\frac{\partial V}{\partial S}\right)_p} \underset{\text{maxwell relation}}{=} \frac{1}{\left(\frac{\partial T}{\partial p}\right)_S} = \left(\frac{\partial p}{\partial T}\right)_S$$

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

Combined 1st + 2nd:

$$dU = TdS - pdV$$

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

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

d) $A(T,V)$

$$\left(\frac{\partial A}{\partial S}\right)_p = \left(\frac{\partial A}{\partial T}\right)_V \left(\frac{\partial T}{\partial S}\right)_p + \left(\frac{\partial A}{\partial V}\right)_T \left(\frac{\partial V}{\partial S}\right)_p$$

Combining 1st + 2nd law:

$$dA = -SdT - pdV$$

Total differential:

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

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

Maxwell relation

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

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p = \left(\frac{\partial H}{\partial S}\right)_p \left(\frac{\partial S}{\partial T}\right)_V + \left(\frac{\partial H}{\partial p}\right)_S \underbrace{\cancel{\left(\frac{\partial p}{\partial T}\right)_p}}_{\to 0}$$

$$\left(\frac{\partial x}{\partial y}\right)_x = 0$$

$$C_p = \underbrace{\left(\frac{\partial H}{\partial S}\right)_p}_{= T} \left(\frac{\partial S}{\partial T}\right)_V$$

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_V$$

$$\Rightarrow \left(\frac{\partial S}{\partial T}\right)_V = \frac{C_p}{T} \quad \Rightarrow \left(\frac{\partial T}{\partial S}\right)_V = \frac{1}{\left(\frac{\partial S}{\partial T}\right)_V} = \frac{T}{C_p}$$

$$\left(\frac{\partial A}{\partial S}\right)_p = -S\,\frac{T}{C_p}\;-\left(\frac{\partial T}{\partial p}\right)_S p$$

$$\boxed{\left(\frac{\partial A}{\partial S}\right)_p = -\,\frac{TS}{C_p}\;-\left(\frac{\partial T}{\partial p}\right)_S p}$$

Problem 5:

a) The fundamental relations for changes in enthalpy and entropy as function of temperature and pressure are

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

$$dS(T,p) = \frac{C_p}{T} dT - \left(\frac{\partial V}{\partial T}\right)_p dp$$

It is common to apply the volume expansivity β and isothermal compressibility κ in order to express the volume partial derivatives:

$$\beta \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \quad \kappa \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$$

The following set of data is available for liquid water:

T [°C]	p [bar]	C_p [J/(mol.K)]	V [cm³/mol]	β [1/K]
25	1	75.305	18.071	256×10^{-6}
25	1000	…..	18.012	366×10^{-6}
50	1	75.314	18.234	458×10^{-6}
50	1000	…..	18.174	568×10^{-6}

Consider that C_p is a weak function of T and that both β and V are weak functions of p.

Calculate the enthalpy and entropy changes of liquid water for a change of state from 1 bar and 25 °C to 1000 bar and 50 °C.

b) Illustrate in a figure the thermodynamic path of the calculation of the change of enthalpy and entropy performed under a).

a) Inserting β and κ

$$dH = C_p dT + \left[V - \beta T V\right] dp$$

$$dS = \frac{C_p}{T} dT - V\beta\, dp$$

Considering that C_p is a weak function of T, and β and V are weak functions of p

=> Assume C_p, β and V to be constant during the change

$$C_p \approx \overline{C_p} = \frac{75{,}305 + 75{,}314}{2} = 75{,}3095 \ \frac{J}{K \cdot mol}$$

$$\beta_T \approx \overline{\beta_T} = \frac{458 + 568}{2} \cdot 10^{-6} = 513 \cdot 10^{-6}\, K^{-1}$$

$$V_T \approx \overline{V_t} = \frac{18{,}234 + 18{,}174}{2} = 18{,}204\ cm^3/mol$$

$$dH = C_p\,dT + \left[V - \beta T V\right] dp$$

$$\int_{H_1}^{H_2} dH = \int_{T_1}^{T_2} C_p\,dT + \int_{p_1}^{p_2} V(1-\beta T_2)\,dp$$

$$\Delta H \approx \langle C_p\rangle (T_2 - T_1) + \langle V\rangle \left(1 - \langle \beta\rangle T_2\right)(p_2 - p_1)$$

$$\Delta H = 75{,}3095\ \frac{J}{\cancel{K}\cdot mol}(323\cancel{K} - 298\cancel{K}) + 18{,}204\ cm^3/mol \cdot \left(1 - 513\cdot 10^{-6}\,\cancel{K^{-1}}\cdot 323\,\cancel{K}\right)(1000\ bar - 1\ bar)$$

$$= 1883\ \frac{J}{mol} + 1517\ \frac{J}{mol}$$

$$\frac{cm^3\cdot bar}{mol} = \frac{10^{-6}m^3\cdot 10^5\,Pa}{mol} = \frac{10^{-1}\,m^3\cdot J/m^3}{mol} = 10^{-1}\ J/mol$$

$$\boxed{\Delta H = 3400\ J/mol}$$

$$dS = \frac{C_p}{T}\,dT - V\beta\,dp$$

$$\int_{S_1}^{S_2} dS = \int_{T_1}^{T_2} \frac{C_p}{T}\,dT - \int_{p_1}^{p_2} V\beta\,dp$$

$$\Delta S \approx \langle C_p\rangle \ln\frac{T_2}{T_1} - \langle V\rangle\langle\beta\rangle(p_2 - p_1)$$

$$= 75{,}3095\ \frac{J}{K\cdot mol}\cdot \ln\left(\frac{323K}{298K}\right) - 18{,}204\ cm^3/mol\cdot 513\cdot 10^{-6}\,K^{-1}(1000\ bar - 1\ bar)$$

$$= 6{,}067\ J/K\cdot mol - 0{,}933\ J/K\cdot mol$$

$$\boxed{\Delta S = 5{,}134\ J/K\cdot mol}$$

b)