

Chapter - 5

CH19BO72

ASSIGNMENT

i) To prove: $C_p = C_v + R$ for an ideal gas

I Show that $u = u(T \text{ only})$ for ideal gas

Consider u in terms of independent properties T, v

$$u = u(T, v)$$

$$du = \left(\frac{\partial u}{\partial T}\right)_v dT + \left(\frac{\partial u}{\partial v}\right)_T dv$$

$$\left[\text{By definition, } C_v = \left(\frac{\partial u}{\partial T}\right)_v \right]$$

$$\left[\text{By fundamental relations : } u = T ds - P dV \right]$$

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

$$\Rightarrow du = C_v dT + \left[T \left(\frac{\partial s}{\partial v}\right)_T - P \right] dv$$

$$\Rightarrow du = C_v dT + \left[T \left(\frac{\partial P}{\partial T}\right)_v - P \right] dV$$

(From Thermodynamic web) \Rightarrow Maxwell's relation

$$\text{For an ideal gas, } P = \frac{RT}{V} \Rightarrow \left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V}$$

$$\Rightarrow du = c_v dT + \left(\frac{RT}{v} - P \right) dv \quad [PV = RT]$$

$$\Rightarrow du = c_v dT \quad \text{for an ideal gas}$$

II : Using I, prove $c_p = c_v + R$ for ideal gas

We have,

$$c_p = \left(\frac{\partial h}{\partial T} \right)_P \quad [\text{Definition of } c_p]$$

$$\Rightarrow c_p = \left(\frac{\partial (u + Pv)}{\partial T} \right)_P \quad [h = u + Pv \rightarrow \text{definition}]$$

$$\Rightarrow c_p = \left(\frac{\partial u}{\partial T} \right)_P + P \left(\frac{\partial v}{\partial T} \right)_P \quad [\text{As } P = \text{constant, we can take } P \text{ out of the derivative}]$$

$$\Rightarrow c_p = \left(\frac{\partial u}{\partial T} \right)_P + R \quad \left[\left(\frac{\partial v}{\partial T} \right)_P = \frac{R}{P} \quad \text{for ideal gas} \right]$$



From I, we know that $u = u(T \text{ only})$

$$\Rightarrow \left(\frac{\partial u}{\partial T} \right)_P = \frac{du}{dT} = c_v$$

$$\Rightarrow \boxed{c_p = c_v + R}$$

2) We have,

$$\left(\frac{\partial h}{\partial T}\right)_S = \left(\frac{T \frac{\partial S}{\partial T} + V \frac{\partial P}{\partial T}}{\frac{\partial T}{\partial T}}\right)_S = V \left(\frac{\partial P}{\partial T}\right)_S$$

Using Maxwell's relation,

$$\left(\frac{\partial h}{\partial T}\right)_S = V \left(\frac{\partial S}{\partial V}\right)_P = V \left(\frac{\partial S}{\partial T}\right)_P \left(\frac{\partial T}{\partial V}\right)_P$$

We have,

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T} \quad (\text{using thermodynamic web})$$

$$\left(\frac{\partial T}{\partial V}\right)_P = \frac{1}{R} \left(\frac{RT}{V-b} - \frac{2a}{V^2} + \frac{2ab}{V^3} \right)$$

(differentiating Van der Waal's EoS)

Substituting above relations,

We have

$$\left(\frac{\partial h}{\partial T}\right)_S = C_P \left[\frac{V}{V-b} - \frac{2a}{VR} \left(1 - \frac{b}{V}\right)^2 \right] \rightarrow (1)$$

We know (From slides \rightarrow we proved it)

$$C_P = C_V + \frac{V T \beta^2}{K} \rightarrow (2)$$

where

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P$$

$$K = \frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T$$

Vanderwaal's eqn

$$P = \frac{RT}{V-b} - \frac{a}{V^2} \Leftrightarrow T = \left(\frac{V-b}{R} \right) \left[P + \frac{a}{V^2} \right]$$

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

$$\left(\frac{\partial T}{\partial V} \right)_P = -\frac{1}{R} \left(\frac{RT}{V-b} - \frac{2a}{V^2} + \frac{2ab}{V^3} \right)$$

$$\Rightarrow \beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = \frac{1}{V} \times \frac{1}{\left(\frac{\partial T}{\partial V} \right)_P} = \frac{R}{V \left(\frac{RT}{V-b} - \frac{2a}{V^2} + \frac{2ab}{V^3} \right)}$$

$$\Rightarrow K = \frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T = \frac{1}{V} \times \frac{1}{\left(\frac{\partial P}{\partial V} \right)_T} = \frac{1}{V \left(\frac{RT}{(V-b)^2} - \frac{2a}{V^3} \right)}$$

Substituting values above in (2)

$$\Rightarrow C_P = C_V + \frac{TR^2}{V \left(\frac{RT}{V-b} - \frac{2a}{V^2} + \frac{2ab}{V^3} \right)^2} \times V \left(\frac{RT}{(V-b)^2} - \frac{2a}{V^3} \right)$$

Substituting above eqn in (1)

$$\Rightarrow \left(\frac{\partial h}{\partial T} \right)_S = \left[C_V + R^2 T \left(\frac{RT}{(V-b)^2} - \frac{2a}{V^3} \right) \right] \left[\frac{V}{V-b} - \frac{2a}{V^2 RT} \left(1 - \frac{b}{V} \right) \right]$$

$\left(\frac{\partial h}{\partial T} \right)_S$ in terms of C_V, R, a, b, T, V

$$3) \left(\frac{\partial T}{\partial P} \right)_S$$

(a) By cyclic rule,

$$\left(\frac{\partial T}{\partial P} \right)_S \left(\frac{\partial P}{\partial S} \right)_T \left(\frac{\partial S}{\partial T} \right)_P = -1$$

$$\Rightarrow \left(\frac{\partial T}{\partial P} \right)_S = - \left(\frac{\partial S}{\partial P} \right)_T \left(\frac{\partial T}{\partial S} \right)_P \rightarrow (1)$$

• By Maxwell's relation,

$$-\left(\frac{\partial S}{\partial P} \right)_T = \left(\frac{\partial V}{\partial T} \right)_P$$

$$\text{ideal gas: } V = \frac{RT}{P} \Rightarrow \left(\frac{\partial V}{\partial T} \right)_P = \frac{R}{P}$$

$$\Rightarrow -\left(\frac{\partial S}{\partial P} \right)_T = \frac{R}{P} \quad \underline{\underline{\quad}} \quad \rightarrow (2)$$

• From the thermodynamic web,

(by the defn of C_P)

$$\left(\frac{\partial S}{\partial T} \right)_P = \frac{C_P}{T}$$

$$\Rightarrow \left(\frac{\partial T}{\partial S} \right)_P = \frac{T}{C_P} \rightarrow (3)$$

Substituting (2) & (3) in (1)

$$\Rightarrow \boxed{\left(\frac{\partial T}{\partial P} \right)_S = \frac{RT}{PC_P} = \frac{V}{C_P}} \rightarrow \text{ideal gas}$$

(b) From (a), we have $\left(\frac{\partial T}{\partial P}\right)_S = \frac{RT}{PC_P}$ for ideal gas

Separating variables and integrating along path $s = \text{constant}$

$$\Rightarrow \int_{T_1}^{T_2} \frac{\partial T}{T} = \frac{R}{C_P} \int_{P_1}^{P_2} \frac{\partial P}{P} \quad (R, C_P \rightarrow \text{constants})$$

s = const

$$\Rightarrow \ln\left(\frac{T_2}{T_1}\right) = \frac{R}{C_P} \ln\left(\frac{P_2}{P_1}\right)$$

$$\Rightarrow \frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{\frac{R}{C_P}}$$

$$\Rightarrow \frac{\frac{P_2 V_2}{R}}{\frac{P_1 V_1}{R}} = \left(\frac{P_2}{P_1}\right)^{\frac{R}{C_P}} \quad [\text{ideal gas eqn}]$$

$$\Rightarrow P_2 \left(1 - \frac{R}{C_P}\right) V_2 = P_1 \left(1 - \frac{R}{C_P}\right) V_1$$

We have,

$$1 - \frac{R}{C_P} = \frac{C_P - R}{C_P} = \frac{C_V}{C_P} = \frac{1}{\Gamma}$$

$$(C_P - C_V = R \text{ for ideal gas})$$

$$\therefore P_2 \frac{1}{\Gamma} V_2 = P_1 \frac{1}{\Gamma} V_1$$

If we raise both sides by Γ power

$$\Rightarrow P_2 V_2^\Gamma = P_1 V_1^\Gamma$$

$$\Rightarrow \boxed{P V^\Gamma = \text{const}}$$

$$\Gamma = \frac{C_P}{C_V}$$

(c) From (a), we obtained

$$\left(\frac{\partial T}{\partial P}\right)_S = \frac{T}{C_P} \left(\frac{\partial V}{\partial T}\right)_P \rightarrow (1)$$

↓

This is the general relation we got ~~in~~ before applying ideal gas law (in part (a))

Vanderwaal's eqn

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

$$\Rightarrow T = \frac{1}{R} \left(P + \frac{a}{V^2}\right)(V - b)$$

$$\Rightarrow \left(\frac{\partial T}{\partial V}\right)_P = \frac{1}{R} \left[\left(P + \frac{a}{V^2}\right)(1) - (V - b) \left(\frac{2a}{V^3}\right) \right]$$

Put $P + \frac{a}{V^2} = \frac{RT}{V-b}$ in above

$$\Rightarrow \left(\frac{\partial T}{\partial V}\right)_P = \frac{RTV^3 - 2a(V-b)^2}{RV^3(V-b)}$$

$$\Rightarrow \left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{\left(\frac{\partial T}{\partial V}\right)_P} = \frac{RV^3(V-b)}{RTV^3 - 2a(V-b)^2}$$

Substituting in (1)

$$\left(\frac{\partial T}{\partial P}\right)_S = \frac{RTV^3(V-b)}{RC_PT V^3 - 2a C_P (V-b)^2}$$

↓

For vanderwaal's gas

4)

$$(a) v_i = \frac{V_i}{n} = \frac{A l_i}{n} = \frac{0.1 \text{ m}^2 \times 0.4 \text{ m}}{250 \text{ mol}} = 1.6 \times 10^{-4} \frac{\text{m}^3}{\text{mol}}$$

$$\begin{aligned} P_i &= P_{\text{atm}} + \frac{mg}{A} = 1.01325 \times 10^5 + \frac{10^4 \times 9.81}{0.1} \\ &= 1.082 \times 10^6 \text{ Pa} \end{aligned}$$

By Vander Waal's equation,

$$\text{we can find } T_i = \left(P_i + \frac{a}{v_i^2} \right) \frac{(v_i - b)}{R}$$

$$\text{Substituting } P_i = 1.082 \times 10^6 \text{ Pa},$$

$$a = 0.5 \text{ J m}^3/\text{mol}^2$$

$$b = 4 \times 10^{-5} \text{ mol/m}^3$$

$$v_i = 1.6 \times 10^{-4} \text{ m}^3/\text{mol}$$

$$R = 8.314 \text{ J/mol-K}$$

$$\text{we obtain } \underline{\underline{T_i = 297.49 \text{ K}}}$$

We have,

$$du = \left(\frac{\partial u}{\partial T} \right)_v dT + \left(\frac{\partial u}{\partial v} \right)_T dv = \left(\frac{\partial u}{\partial v} \right)_T dv$$

(since process is isothermal)

$$\Rightarrow du = \cancel{\left(\frac{\partial u}{\partial T} \right)} \left(\frac{T \partial S - P \partial V}{\partial V} \right)_T dv$$

(Fundamental property relations)

$$\Rightarrow du = \left[T \left(\frac{\partial s}{\partial v} \right)_T - p \right] dv$$

$$du = \left[T \left(\frac{\partial p}{\partial T} \right)_v - p \right] dv \quad (\text{Maxwell's relation})$$

From Vanderwaal's eqn ,

$$p = \frac{RT}{v-b} - \frac{a}{v^2}$$

$$\left(\frac{\partial p}{\partial T} \right)_v = \frac{R}{v-b}$$

$$\Rightarrow du = \left(\frac{TR}{v-b} - p \right) dv$$

$$\Rightarrow \Delta u = \int_{v_1}^{v_2} \left(\frac{RT}{v-b} - p \right) dv = \int_{v_1}^{v_2} \frac{a}{v^2} dv$$

(For Vanderwaal's eqn)

To find v_2

Assumption : Gas in state (2) is an ideal gas

since $P_2 \approx$ atmospheric pressure

$$\Rightarrow v_2 = \frac{RT_2}{P_2} \quad \left[T_2 = T_1 = 297.49 \text{ K} \right. \\ \left. P_2 = P_{\text{atm}} = 1.01325 \times 10^5 \text{ Pa} \right]$$

$$\Rightarrow v_2 = 0.0244 \text{ m}^3/\text{mol}$$

Substituting in eqn put Δu

$$\Rightarrow \Delta u = \int_{1.6 \times 10^{-4}}^{0.0244} \frac{0.5}{v^2} dv = 3104.5 \text{ J/mol}$$

$$\Rightarrow \Delta U = \Delta u \times \text{no. of moles}$$
$$= 3104.5 \times 250$$

$$\boxed{\Delta U = 776.125 \text{ kJ}}$$

(b) $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{sur}}$

ΔS_{system}

$$S_{\text{sys}} = s(T, v)$$

$$dS_{\text{sys}} = \left(\frac{\partial s}{\partial T}\right)_v dT + \left(\frac{\partial s}{\partial v}\right)_T dv$$

$$dS_{\text{sys}} = \left(\frac{\partial s}{\partial v}\right)_T dv \quad (\text{since it is isothermal})$$

$$dS_{\text{sys}} = \left(\frac{\partial P}{\partial T}\right)_v dv \quad [\text{Maxwell's relation}]$$

$$dS_{\text{sys}} = \frac{R}{v-b} dv \quad (\text{Vanderwaal's gas})$$

$$\cancel{\Delta S_T} \quad \cancel{\Delta S_{\text{sys}}} = \int_{v_1}^{v_2} \frac{R}{v-b} dv$$

$$= \int_{1.6 \times 10^{-4}}^{0.0244} \frac{8.314}{v - 4 \times 10^{-5}} dv$$

$$\Rightarrow \Delta S_{\text{system}} = 44.17 \frac{\text{J}}{\text{mol} \cdot \text{K}}$$

$$\Rightarrow \Delta S_{\text{system}} = n \times \Delta s_{\text{system}} = 250 \times 44.17$$

$$\underline{\underline{\Delta S_{\text{system}} = 11042.5 \text{ J/K}}}$$

$\Delta S_{\text{surroundings}}$

$$\Delta S_{\text{surv}} = \frac{Q_{\text{surv}}}{T_{\text{surv}}} = -\frac{Q}{T_{\text{surv}}} \quad (Q = \text{heat transfer for system})$$

$$\text{First law of Thermodynamics} \Rightarrow Q = \Delta U - W$$

$$\Delta U = 776.125 \text{ kJ (From (a))}$$

$$\Delta W = -n \int_{V_1, \text{act}}^{V_2} P dV \rightarrow$$

$$P_{\text{act}} = \text{constant} = P_{\text{atm}}$$

$$\Rightarrow \Delta W = -n P_{\text{atm}} (V_2 - V_1)$$

$$= -250 \times 1.01325 \times 10^5 (0.0244 - 1.6 \times 10^{-4})$$

$$\underline{\underline{W = -614030 \text{ J}}}$$

$$\Rightarrow Q = 776125 + 614030 = \underline{\underline{1.39 \times 10^6 \text{ J}}}$$

$$T_{\text{surv}} = T = \text{constant} = 297.49 \text{ K}$$

$$\Rightarrow \Delta S_{\text{surv}} = \frac{-Q}{T_{\text{surv}}} = \frac{-1.39 \times 10^6}{297.49} = \underline{\underline{-4673 \frac{\text{J}}{\text{K}}}}$$

$$\therefore \Delta S_{\text{univ}} = \Delta S_{\text{system}} + \Delta S_{\text{surv}}$$

$$= 11042.5 \frac{\text{J}}{\text{K}} - 4673 \frac{\text{J}}{\text{K}}$$

$$\boxed{\Delta S_{\text{univ}} = 6369.5 \frac{\text{J}}{\text{K}}}$$

5)



(a) We have C_V values for ideal gas only.
So we need to relate C_V real with C_V ideal

~~$$C_V \text{ real} = C_V(T, V_0)$$~~

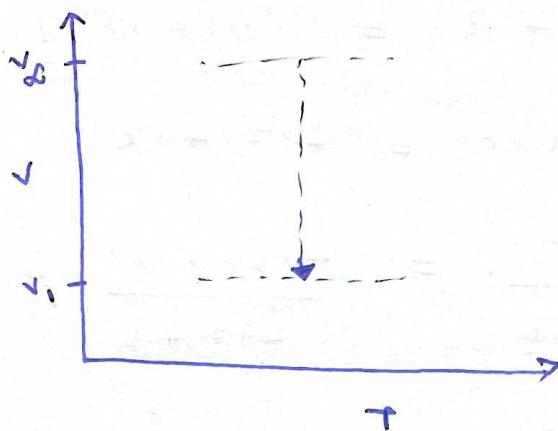
$$C_V \text{ real} = C_V \text{ ideal} + \int_{V_{\text{ideal}}}^{V_{\text{real}}} \left[T \left(\frac{\partial^2 P}{\partial T^2} \right)_V \right] dV$$



This relation is given in the textbook

Proof of the above relation

Consider the below path:



We use the constant temperature path

$$\Rightarrow \frac{dc_v}{dv} = \left(\frac{\partial c_v}{\partial v} \right)_T = \left[\frac{\partial}{\partial v} \left(\frac{\partial u}{\partial T} \right)_v \right]_T = \left[\frac{\partial}{\partial T} \left(\frac{\partial u}{\partial v} \right)_T \right]_v$$

$$= \left[\frac{\partial}{\partial T} \left(T \left(\frac{\partial P}{\partial T} \right)_v - P \right) \right]_v$$

$$= \left(\frac{\partial P}{\partial T} \right)_v + T \left(\frac{\partial^2 P}{\partial T^2} \right)_v - \left(\frac{\partial P}{\partial T} \right)_v = T \left(\frac{\partial^2 P}{\partial T^2} \right)_v$$

$$\Rightarrow \int_{c_v \text{ ideal}}^{c_v \text{ real}} dc_v = \int_{v_{\text{ideal}}}^v T \left(\frac{\partial^2 P}{\partial T^2} \right)_v dv$$

$$\Rightarrow c_v \text{ real} = c_v \text{ ideal} + \int_{v_{\text{ideal}}}^v T \left(\frac{\partial^2 P}{\partial T^2} \right)_v dv$$

Vanderwaal's eqn,

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

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

$$\left(\frac{\partial P^2}{\partial T^2} \right)_v = 0$$

$$\Rightarrow c_v \text{ real} = c_v \text{ ideal}$$

$$= c_p \text{ ideal} - R$$

$$= R \left[3.376 + 0.557 \times 10^{-3} T - \frac{3100}{T^2} \right] - R$$

(T = 500 K at initial state)

$$\Rightarrow C_{V,\text{real}} = 8.314 \left[3.376 + 0.557 \times 10^{-3} (500) - \frac{3100}{500^2} - 1 \right]$$

$$\Rightarrow C_{V,\text{real}} = 21.96 \frac{\text{J}}{\text{mol}\cdot\text{K}}$$

(b) Consider the entire tank as system

$$w = 0 \quad [\text{volume of entire } (2L) \text{ tank} = \text{const}]$$

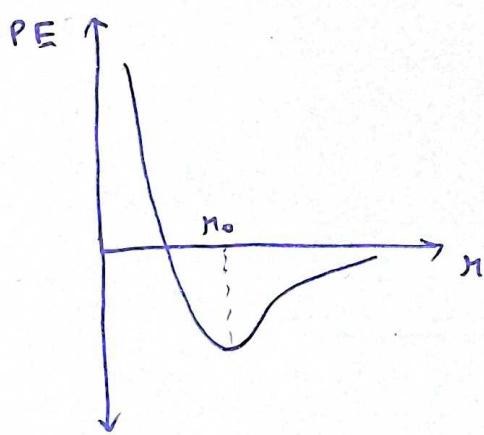
$$Q = 0 \quad (\text{insulated setup})$$

$$\Rightarrow \text{From First law, } \Delta U = 0 \quad [\Delta U = Q + w]$$

$$\Delta U \rightarrow \text{internal PE} + \text{internal KE}$$

As diaphragm ruptures, volume available to the molecules increases, therefore intermolecular distance \uparrow

\Rightarrow ~~isolated~~



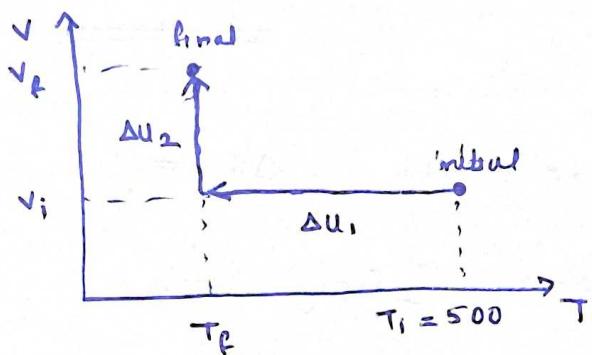
At $n > n_0$,
as $n \uparrow$, PE \uparrow

i.e. as intermolecular distance in the region \uparrow ,
intermolecular PE \uparrow
Since $\Delta U = 0$, ~~intermolecular~~ molecular KE \downarrow
(to cancel the effect)

Temperature is a manifestation of molecular KE

∴ Temperature decreases ~~decreases~~ decreases

(c) We create a two step hypothetical path



$\Delta U_1 \Rightarrow$ constant volume path $\Delta U_2 \Rightarrow$ const. temperature path

$$\Delta U_1 = \int_{T_i}^{T_f} C_V \text{real} \, dT = \int_{T_i}^{T_f} C_V \text{ideal} \, dT$$

$$= R \int_{500}^{T_f} \left(3.376 + 0.557 \times 10^{-3} T - \frac{3100}{T^2} - 1 \right) dT$$

$$= (2.32 \times 10^{-3}) T_f^2 + (19.75) T_f + \frac{25773.4}{T_f} - 10507.4$$

$$\Delta U_2 = \int_{V_i}^{V_f} \left(\frac{\partial u}{\partial v} \right)_T \, dv = \int_{V_i}^{V_f} \left[T \left(\frac{\partial P}{\partial T} \right)_v - P \right] \, dv$$

$$\left(\frac{\partial P}{\partial T} \right)_v = \frac{R}{v-b} \quad \text{for van der waals EOS}$$

$$= \int_{0.001}^{0.002} \left(\frac{RT}{v-b} - P \right) \, dv = \int_{0.001}^{0.002} \frac{a}{v^2} \, dv$$

a for CO ($T_c = 132.9 \text{ K}$, $P_c = 34.96 \times 10^{-5} \text{ Pa}$)

$$a = \frac{27}{64} \frac{R^2 T_c^2}{P_c} = 0.1473$$

$$\therefore \Delta u_2 = \int_{0.001}^{0.002} \frac{0.1473}{v^2} dv = 73.7 \frac{\text{J}}{\text{mol}}$$

We proved in (b) that $\Delta u = 0$

$$\Delta u = \Delta u_1 + \Delta u_2 = 0 \quad [\text{Only 1 mole CO, } \therefore \Delta u = \Delta u_1]$$

$$\Rightarrow (2.32 \times 10^{-3}) T_f^2 + 19.75 T_f + \frac{25773.4}{T_f} - 10507.4 + 73.7 = 0$$

The above equation can be solved numerically

to get $\underline{T_f = 49 \text{ K}}$

(d) $\Delta s_{\text{surv}} = \Delta s_{\text{sys}} + \Delta s_{\text{surv}}$

↓

0 (since $Q_{\text{surv}} = 0 \rightarrow \text{well insulator}$)

$$ds_{\text{sys}} = \left(\frac{\partial s}{\partial T} \right)_V dT + \left(\frac{\partial s}{\partial V} \right)_T dv$$

↓

↓

$$\frac{C_V}{T} \quad \left(\frac{\partial P}{\partial T} \right)_V = \frac{R}{V-b} \quad (\text{for Van der Waal EOS})$$

(Thermodyn. web)

$$ds_{\text{sys}} = \frac{C_V}{T} dT + \frac{R}{V-b} dv$$

$$\Delta S_{sys} = \int_{500K}^{497K} \frac{C_v}{T} dT + \int_{0.001}^{0.002} \frac{R}{(v-b)} dv$$

$$= R \left[\int_{500K}^{497K} \left(\frac{2.376}{T} + 0.557 \times 10^{-3} - \frac{3100}{T^3} \right) dT + \int_{0.001}^{0.002} \frac{dv}{v - 3.95 \times 10^{-5}} \right]$$

$$= 5.80 \frac{J}{mol \cdot K}$$

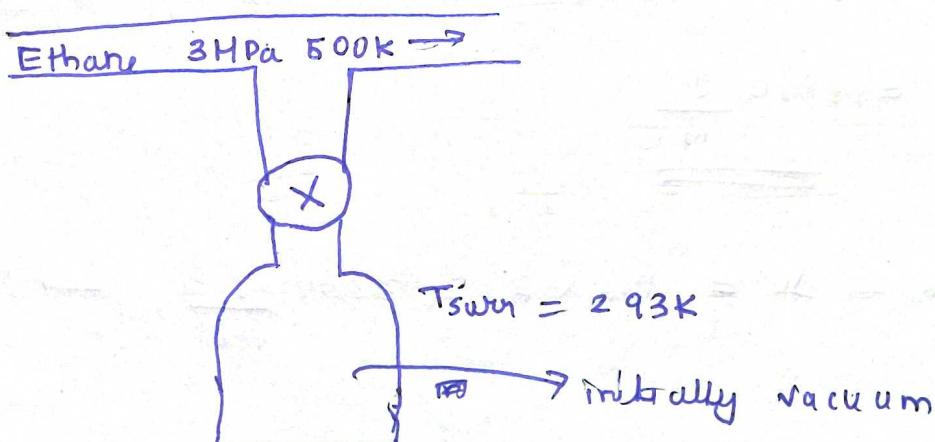
$$\therefore \Delta S_{univ} = 5.80 \frac{J}{mol \cdot K}$$

b for CO

$$b = \frac{RT_c}{8P_c} = 3.95 \times 10^{-5}$$

$$\Delta S_{univ} = \Delta S_{univ} \times 1 \text{ mole} = 5.80 \frac{J}{K}$$

6)



(a) Consider tank as system

Transient energy balance:
(macroscopic KE, PE neglected)

$$\left(\frac{du}{dt}\right)_{sys} = \sum_{in} \dot{n}_{in} h_{in} - \sum_{out} \dot{n}_{out} h_{out} + \dot{Q} + \dot{W}_s$$

(adiabatic process, no shaft work given)

only one inlet

$$\Rightarrow \left(\frac{du}{dt}\right)_{sys} = \dot{n}_{in} h_{in}$$

$$\Rightarrow \int_{u_1}^{u_2} du = \dot{n}_{in} \int_0^t h_{in} dt$$

$$u_2 - u_1 = (\dot{n}_2 - \dot{n}_1) h_{in}$$

($\dot{n}_1 = 0$ since initially vacuum)

$$\Rightarrow \underline{\underline{u_2 = h_{in}}}$$

$$u_2 = u_{in} + P_{in} V_{in} \quad (\text{definition of } h) \quad \cancel{500}$$

$$u_2 \rightarrow u \text{ at } 3 \text{ MPa, T}$$

$$u_{in} \rightarrow u \text{ at } 3 \text{ MPa, } 500 \text{ K}$$

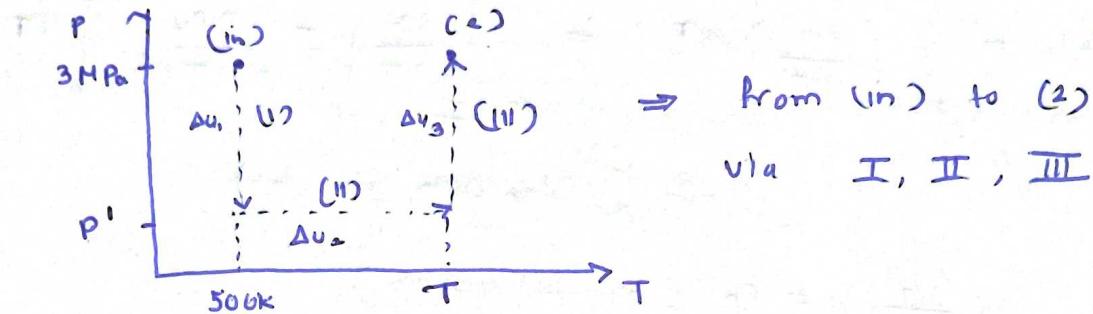
$$P_{in} V_{in} = R T_{in} (1 + B' P_{in}) \quad [T_{in} = 500 \text{ K}, P_{in} = 3 \text{ MPa}]$$

$$= 8.314 \times 500 \left(1 + -2.8 \times 10^{-9} \times 3 \times 10^6\right) \frac{\text{J}}{\text{mol}}$$

$$\underline{\underline{= 3800 \frac{\text{J}}{\text{mol}}}}$$

$$u_2 - u_{in} = \Delta u = P_{in} V_{in} = 3800 \frac{\text{J}}{\text{mol}} \rightarrow (1)$$

Next we need to find $u_2 - u_{in}$



I and III (Take $P' = \text{low } P \rightarrow 0$)

conut T

$$\Rightarrow \frac{du}{dp} = \left(\frac{\partial u}{\partial p} \right)_T = T \left(\frac{\partial s}{\partial p} \right)_T - p \left(\frac{\partial v}{\partial p} \right)_T$$

$$= -T \left(\frac{\partial v}{\partial T} \right)_p + p \left(\frac{\partial v}{\partial p} \right)_T \quad \rightarrow (\text{Thermo, Web})$$

$$PV = RT(1 + B'P)$$

$$\left(\frac{\partial v}{\partial T} \right)_p = \frac{R}{p} (1 + B'p)$$

$$\left(\frac{\partial v}{\partial p} \right)_T = RT \left(\frac{-1}{p^2} \right)$$

$$\Rightarrow \left(\frac{\partial u}{\partial p} \right)_T = -\frac{RT}{p} (1 + B'p) + \Phi \frac{RT}{p} = -B'RT$$

∴

$$\Delta u_1 = \int_{P_{in}}^0 \left(\frac{\partial u}{\partial p} \right)_T dp = - \int_{P_{in}}^0 B'RT dp = B'RT P_{in}$$

$$= -2.8 \times 10^{-8} \times 8.314 \times 500 \times 3 \times 10^6 = -\underline{\underline{349 \text{ J/mol}}}$$

$$\Delta u_3 = \int_0^{P_{in}} \left(\frac{\partial u}{\partial p} \right)_T dp = -B'RT P_2 = 2.8 \times 10^{-8} \times 8.314 \times T \times 3 \times 10^6$$

$$= \underline{\underline{0.7T}}$$

II

$$\Delta u_2 = \int_{500}^T \left(\frac{\partial u}{\partial T} \right)_p dT = \int_{500}^T \left[\left(\frac{\partial h}{\partial T} \right)_p - \left(\frac{\partial Pv}{\partial T} \right)_p \right] dT$$

(definition of h)

$$\left(\frac{\partial h}{\partial T} \right)_p = c_p \text{ (by definition)}$$

$\left(\frac{\partial Pv}{\partial T} \right)_p \Rightarrow$ (since P is low, we can take ideal gas assumption)

$$\therefore \left(\frac{\partial Pv}{\partial T} \right)_p = R$$

$$\Delta u_2 = \int_{500}^T (c_p - R) dT = R \int_{500}^T (0.131 + 19.225 \times 10^{-3} T - 5.561 \times 10^{-6} T^2) dT$$

Substituting Δu_1 , Δu_2 , Δu_3 into (1)

$$\Rightarrow \Delta u = \Delta u_1 + \Delta u_2 + \Delta u_3 = 3800 \frac{J}{mol}$$

$$-349 \frac{J}{mol} + 0.7T + R \int_{500}^T (0.131 + 19.225 \times 10^{-3} T - 5.561 \times 10^{-6} T^2) dT = 3800 \frac{J}{mol}$$



Solving the above eqn for T

$$\Rightarrow T = 552 K \quad (\text{Temperature immediately after } \underline{\text{valve is closed}})$$

(b) Finding final pressure

Finding molar volume v

$$v = \frac{RT}{P} (1 + B' P) \rightarrow \text{when the value is just closed}$$

$$= \frac{8.314 \times 552}{3 \times 10^6} (1 - 2.8 \times 10^{-8} \times 3 \times 10^6 P)$$

$$v = 0.0014 \text{ m}^3/\text{mol}$$

As tank walls, volume of tank will not change (neglect small variations)

No. of moles of ethane is also fixed

$\rightarrow v = \boxed{\text{constant}}$

$$v = 0.0014 = \frac{(8.314)(293)}{P_2} (1 - 2.8 \times 10^{-8} P_2)$$

↳ when it is stored at 293 K

Solving above,

$$P_2 = 1.66 \times 10^6 \text{ Pa}$$

Finding ΔS_{system}

$$dS_{\text{sys}} = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

$$= \frac{C_P}{T} dT + \left(\frac{\partial V}{\partial T}\right)_P dP \quad (\text{Thermo. web})$$



$$\frac{R(1+B'P)}{P} \quad (\text{EOS})$$

$$\Delta S_{\text{system}} = R \int_{293K}^{552K} \left(\frac{1.131}{T} + 19.225 \times 10^{-3} - 5.5 \times 10^{-6} T \right) dT$$

$$+ R \int_{3 \times 10^6 \text{ Pa}}^{1.66 \times 10^6 \text{ Pa}} \left(\frac{1}{P} + B' \right) dP$$

$$= R (-5.087 + -0.554)$$

$$\underline{\Delta S_{\text{sys}} = -46.9 \frac{J}{\text{mol}\cdot\text{K}}}$$

Finding ΔS_{surv}

$$\text{1st law: } \Delta U + q < q \quad (\text{since } w=0)$$

↓
volume does not change

$$\Rightarrow \Delta h - \Delta(PV) = q$$

$$\Rightarrow q = \int_{T_i}^{T_f} c_p^{\text{real}} dT - v(P_f - P_i) \quad (\text{molar volume is const})$$

$$\Rightarrow q = \int_{T_i}^{T_f} c_p^{\text{ideal}} dT - v(P_f - P_i) \quad \text{G}$$

$$\overline{c_p^{\text{real}}} = c_p^{\text{ideal}} - \int_{P_i^{\text{real}}}^{P_f^{\text{real}}} \left[T \left(\frac{\partial^2 v}{\partial T^2} \right)_P \right] dP$$

$$\text{G} \quad v = \frac{RT}{P} (1 + B'P)$$

$$\frac{\partial v}{\partial T} = \frac{R}{P} (1 + B'P)$$

$$\frac{\partial^2 v}{\partial T^2} = 0$$

$$\Rightarrow c_p^{\text{real}} = c_p^{\text{ideal}}$$

]

$$\Rightarrow q = R \int_{552K}^{293K} (1.131 + 19.225 \times 10^{-3}T - 5.561 \times 10^{-6}T^2) dT$$

$$-(0.0014) [1.66 \times 10^6 - 3 \times 10^4]$$

$$\Rightarrow q = -15845 \frac{J}{mol}$$

$$\Rightarrow q_{\text{sum}} = -q = 15845 \frac{J}{mol}$$

$$\Rightarrow \Delta S_{\text{univ}} = \frac{q_{\text{sum}}}{T_{\text{sum}}} = \frac{15845}{293} = 54.08 \frac{J}{mol \cdot K}$$

Finding no. of moles in the tank ($C = \text{constant}$)

$$n = \frac{\sqrt{V}}{v} = \frac{0.05}{0.0014} = 75.7 \text{ mol}$$

$$\Rightarrow \Delta S_{\text{univ}} = n(\Delta S_{\text{sys}} + \Delta S_{\text{sum}})$$

$$= 75.7 (-46.9 + 54.08)$$

$$= \underline{\underline{54.4 \frac{J}{K}}}$$

7)

State - 1

$$T = 300\text{ K} \quad P = 30 \text{ bar}$$

State - 2

$$T = 400\text{ K} \quad P = 50 \text{ bar}$$

$(T_c = 305.4 \text{ K}, \quad P_c = 48.74 \text{ bar}) \rightarrow \text{from table}$

ethane

$$P_{1n} = \frac{30}{P_c} = \frac{30}{48.74} = 0.616 \quad P_{2n} = \frac{50}{48.74} = 1.026$$

$$T_{1n} = \frac{T}{T_c} = \frac{300}{305.4} = 0.982 \quad T_{2n} = \frac{400}{305.4} = 1.31$$

$$\omega (\text{of ethane}) = 0.099$$

(a)

Enthalpy

$$\text{Table C}_3 \quad \left(\left(\frac{\Delta h^{\text{dip}}}{RT_c} \right)^{(0)} \right)$$

| | 0.6 | 0.7 |
|------|--------|--------|
| 0.98 | -0.797 | -1.002 |
| 0.99 | -0.773 | -0.964 |

$$P_{1n} = 0.616$$

$$T_{1n} = 0.982$$

Double interpolation

$$\Rightarrow \left[\frac{\Delta h^{\text{dip}}}{RT_c} \right]^{(0)} = -0.825$$

| | P _{2n} |
|---|-----------------|
| 1 | 1.1 |

$$P_{2n} = 1.026$$

$$T_{2n} = 1.31$$

Double interpolation

| | -0.698 | -0.778 |
|-----|--------|--------|
| 1.3 | -0.518 | -0.652 |

$$\Rightarrow \left[\frac{\Delta h^{\text{dip}}}{RT_c} \right]^{(0)} = -0.711$$

(Table C₃, C₄, C₅, C₆ → according to Koretsky)

$$\text{Table C}_4 \left(\left[\frac{\Delta h_{T_H, P_H}^{\text{dip}}}{R T_C} \right]^{(1)} \right)$$

$$P_{1H} = 0.616 \quad T_{1H} = 0.982$$

P_{1H}

$$0.6 \quad 0.7$$

Double interpolation

| | | | |
|----------|------|--------|--------|
| T_{1H} | 0.98 | -0.776 | -0.994 |
| | 0.99 | -0.722 | -0.908 |

$$\Rightarrow \left[\frac{\Delta h_{T_{1H}, P_{1H}}^{\text{dip}}}{R T_C} \right]^{(1)} = -0.799$$

$$P_{2H} = 1.026 \quad T_{2H} = 1.31$$

P_{2H}

$$1 \quad 1.1$$

Double interpolation

| | | | |
|----------|-----|--------|--------|
| T_{2H} | 1 | -0.203 | -0.212 |
| | 1.1 | -0.111 | -0.114 |

$$\Rightarrow \left[\frac{\Delta h_{T_{2H}, P_{2H}}^{\text{dip}}}{R T_C} \right]^{(1)} = -0.196$$

Using all the values above, we can find departure functions at (1) and (2) (and mi w)

$$\begin{aligned} \frac{\Delta h_{T_H, P_H}^{\text{dip}}}{R T_C} &= \left[\frac{\Delta h_{T_H, P_H}^{\text{dip}}}{R T_C} \right]^{(1)} + w \left[\frac{\Delta h_{T_H, P_H}^{\text{dip}}}{R T_C} \right]^{(2)} \\ &= -0.825 + 0.099 \times (-0.799) \\ &= \underline{\underline{-0.904}} \end{aligned}$$

$$\begin{aligned} \frac{\Delta h_{T_{2H}, P_{2H}}^{\text{dip}}}{R T_C} &= -0.711 + 0.094 \times (-0.196) \\ &= \underline{\underline{-0.730}} \end{aligned}$$

$$\begin{aligned} \Delta h_{T_1 \rightarrow T_2}^{\text{ideal}} &= \int_{300K}^{400K} c_p dT = R \int_{300}^{400} 1.131 + 19.225 \times 10^{-3} T - 5.561 \times 10^{-6} T^2 dT \\ &= 717.39R \end{aligned}$$

\Rightarrow Total enthalpy change

$$= \Delta h = -\Delta h_{T_{1H}, P_{1H}}^{\text{dip}} + \Delta h_{T_1 \rightarrow T_2}^{\text{idet}} + \Delta h_{T_{2H}, P_{2H}}^{\text{dip}}$$

$$= R [-(-0.904 T_C) + 717.39 + (-0.730 T_C)]$$

$$(T_C = 305.4 \text{ K})$$

$$\Rightarrow \boxed{\Delta h = 6406.2 \frac{\text{J}}{\text{mol}}}$$

(b) Entropy

$$\text{Table C}_5 : \left(\left[\frac{\Delta s^{\text{dip}}}{R \cdot 100} \right]^{(0)} \right)$$

| | | P _{1H} |
|--|------|--------------------|
| | | 0.6 0.7 |
| | | 0.98 0.99 |
| | 0.98 | -0.580 -0.743 |
| | 0.99 | -0.555 -0.705 |

$$\xrightarrow{\text{Double interpolation}} \left[\frac{\Delta s^{\text{dip}}}{R \cdot 100} \right]^{(0)} = -0.601$$

| | | P _{2H} |
|--|-----|--------------------|
| | | 1 1.1 |
| | | 1.3 1.4 |
| | 1.3 | -0.485 -0.431 |
| | 1.4 | -0.303 -0.337 |

$$\xrightarrow{\text{Double interpolation}} \left[\frac{\Delta s^{\text{dip}}}{R \cdot 100} \right]^{(0)} = -0.394$$

$$\text{Table C}_6 : \left[\frac{\Delta s^{\text{dip}}}{R \cdot 100} \right]^{(1)}$$

| | | P _{1H} |
|--|------|--------------------|
| | | 0.6 0.7 |
| | | 0.98 0.99 |
| | 0.98 | -0.734 -0.946 |
| | 0.99 | -0.680 -0.859 |

$$\xrightarrow{\text{Double interpolation}} \left[\frac{\Delta s^{\text{dip}}}{R \cdot 100} \right]^{(1)} = -0.756$$

$$\begin{array}{c}
 P_{2n} \\
 \text{---} \\
 \begin{array}{cc}
 1 & 1.1 \\
 \hline
 T_{2n} & \left[\begin{array}{cc} -0.226 & -0.241 \\ -0.158 & -0.168 \end{array} \right] \\
 1.3 & \\
 1.4 &
 \end{array}
 \end{array}
 \Rightarrow \left[\frac{\Delta s_{\text{dip}}}{T_{2n}, P_{2n}} \right] = \underline{-0.224}$$

using all the values above, and $w = 0.099$

$$\cancel{\Delta s_{\text{dip}}} \left[\frac{\Delta s_{\text{dip}}}{T_{1n}, P_{1n}} \right] = -0.601 + 0.099 \times (-0.756) \\
 = \underline{\underline{-0.676}}$$

$$\left[\frac{\Delta s_{\text{dip}}}{T_{2n}, P_{2n}} \right] = -0.394 + 0.099 \times (-0.224) \\
 = \underline{\underline{-0.416}}$$

$$\begin{aligned}
 \Delta s^{\text{ideal}} &= \cancel{R} \int_{T_1}^{T_2} \frac{C_p}{T} dT - R \ln \left(\frac{P_2}{P_1} \right) \\
 &= R \left[\int_{300}^{400} \frac{1.131 + 19.225 \times 10^{-3}T - 5.541 \times 10^{-6}T^2}{T} dT \right. \\
 &\quad \left. - \ln \left(\frac{50 \text{ bar}}{30 \text{ bar}} \right) \right] = \underline{\underline{1.542 R}}
 \end{aligned}$$

\Rightarrow Total entropy change

$$\begin{aligned}
 \Delta s &= -\Delta s_{T_{1n}, P_{1n}}^{\text{dip}} + \Delta s^{\text{ideal}} + \Delta s_{T_{2n}, P_{2n}}^{\text{dip}} \\
 &= R(+0.676 + 1.542 - 0.416)
 \end{aligned}$$

$$\boxed{\Delta s = 14.98 \frac{\text{J}}{\text{mol-K}}}$$

8) Minimum work \Rightarrow reversible process

reversible + adiabatic $\Rightarrow \Delta S = 0$

$$\Rightarrow -\Delta S_{T_{in}, P_{in}}^{\text{dip}} + \Delta S_{\text{ideal}} + \Delta S_{T_{2n}, P_{2n}}^{\text{dip}} = 0$$

(I) (II) (III)

Methane $\Rightarrow P_c = 46 \text{ bar}$ $T_c = 190.6 \text{ K}$ $w = 0.008$

$$P_{in} = \frac{P_1}{P_c} = \frac{1}{46} = 0.0217$$

$$T_{in} = \frac{T_1}{T_c} = \frac{300 \text{ K}}{190.6 \text{ K}} = 1.57$$

$$P_{2n} = \frac{P_2}{P_c} = \frac{10}{46} = 0.217$$

$$T_{2n} = \frac{T}{T_c} = \frac{T}{190.6 \text{ K}}$$

Term I

Using P_{in} , T_{in} and Table C_f, C_g we can find

$\frac{\Delta S^{\text{dip}}}{R}$ (similar to Q_f) :

$$\left[\frac{\Delta S_{T_{in}, P_{in}}^{\text{dip}}}{R} \right]^{(0)} = -0.00457$$

$$\left[\frac{\Delta S_{T_{2n}, P_{2n}}^{\text{dip}}}{R} \right]^{(1)} = -0.0028$$

$$\Rightarrow \frac{\Delta S_{T_{in}, P_{in}}^{\text{dip}}}{R} = -0.00457 + 0.008 (-0.0028)$$
$$= \underline{-0.0046}$$

Term II

$$\Delta S_{\text{ideal}} = R \left[\int_{T_1=300}^{T_2} C_p dT - \ln \left(\frac{P_2}{P_1} \right) \right]$$

$$= R \left[\int_{300}^{T_2} \frac{1.702 + 9.081 \times 10^{-3} T - 2.164 \times 10^{-6} T^2}{T} dT - \ln \left(\frac{10}{1} \right) \right]$$

Substituting term I & II,

$$\Rightarrow \Delta S = R \left[0.0046 + \int_{300}^{T_2} \frac{1.702 + 9.081 \times 10^{-3} T - 2.164 \times 10^{-6} T^2}{T} dT - 2.803 + \left[\frac{\Delta S_{\text{dip}}}{\frac{T_2 n, P_2 n}{R}} \right] \right] = 0$$

We use trial-and-error method to find the value of T_2 which makes $\Delta S = 0$

We find that, when $T_2 = 379 \text{ K}$,

$$T_{2n} = 1.09, \Delta S = -0.018$$

\therefore we take $\underline{T_2 \approx 379 \text{ K}}$ (as ΔS is close to 0)

Energy balance (steady state, $Q=0$ (adiabatic))

no macroscopic KE, PE)

$$h_1 - h_2 + \overset{\oplus}{w_s} = 0 \Rightarrow \underline{\underline{w_s}} = \underline{\Delta h}$$

Now, we can calculate Δh using

~~the~~ enthalpy departure functions

Using tables C₃ and C₄,

and using $P_{1n} = 0.0217 \quad T_{1n} = 1.57$

$P_{2n} = 0.217 \quad T_{2n} = 1.99$

(By double interpolating), \rightarrow similar to Q?

$$\left[\frac{\Delta h_{\text{dip}}}{R T_c} \right]^{(0)} = \underline{\underline{-0.095}} \quad \left[\frac{\Delta h_{\text{dip}}}{R T_c} \right]^{(1)} = \underline{\underline{-0.011}}$$

$$\left[\frac{\Delta h_{\text{dip}}}{R T_c} \right]^{(0)} = \underline{\underline{-0.0614}} \quad \left[\frac{\Delta h_{\text{dip}}}{R T_c} \right]^{(1)} = \underline{\underline{0.015}}$$

w of methane = 0.008

$$\Rightarrow \left[\frac{\Delta h_{\text{dip}}}{R T_c} \right] = -0.095 + 0.008(-0.011) = \underline{\underline{-0.0966}}$$

$$\left[\frac{\Delta h_{\text{dip}}}{R T_c} \right] = -0.0614 + 0.008(0.015) = \underline{\underline{-0.0613}}$$

$$\Delta h^{\text{ideal}} = R \int C_p dT$$

$$= R \int_{300K}^{379K} 1.702 + 9.081 \times 10^{-3}T - 2.164 \times 10^{-6}T^2 dT$$

$$\Rightarrow \Delta h = -\Delta h_{T_{1n}, P_{1n}}^{\text{dip}} + \Delta h^{\text{ideal}} + \Delta h_{T_{2n}, P_{2n}}^{\text{dip}}$$

$$= R \left[T_c (0.0966 - 0.0613) + \int_{300}^{379} 1.702 + 9.081 \times 10^{-3}T - 2.164 \times 10^{-6}T^2 dT \right]$$

($T_c = 190.6 \text{ K}$ for methane)

$$\Rightarrow \underline{\underline{\Delta h = 3034.2 \text{ J/mol}}}$$

$$\dot{w}_s = \Delta h = 3034.2 \frac{\text{J}}{\text{mol}}$$

$$\begin{aligned}\dot{w}_s &= \dot{m} \times w_s = \frac{2 \text{ mol}}{\text{min}} \times 3034.2 \frac{\text{J}}{\text{mol}} \\ &= \frac{1}{30} \frac{\text{mol}}{\text{s}} \times 3034.2 \frac{\text{J}}{\text{mol}} \\ &= 101.1 \text{ W}\end{aligned}$$
