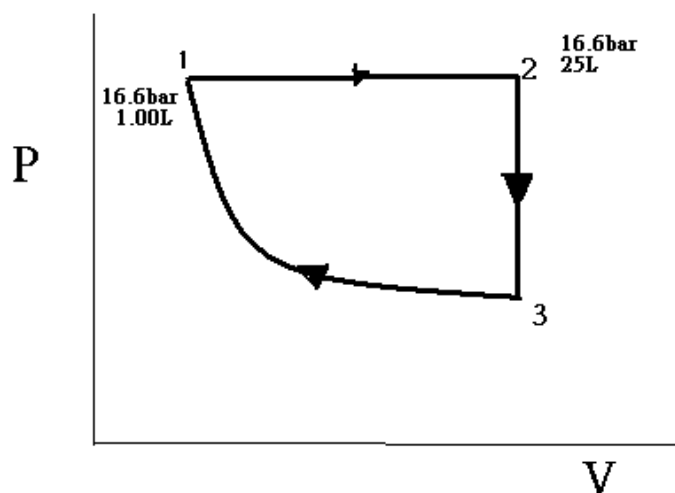


1.



$$N=2 \text{ mol} \quad C_{v,m}=20.79 \text{ J mol}^{-1} \text{ K}^{-1}=\frac{5}{2}R \quad C_{p,m}=29.10 \text{ J mol}^{-1} \text{ K}^{-1}=\frac{7}{2}R$$

$$P_1=16.6 \text{ bar} \quad V_1=1 \text{ L} \quad T_1=\frac{16.6 \text{ bar} \times 1 \text{ L}}{2 \text{ mol} \times 0.08314 \text{ bar L mol}^{-1} \text{ K}^{-1}}=99.83 \text{ K}$$

$$P_2=16.6 \text{ bar} \quad V_2=25 \text{ L} \quad T_2=\frac{16.6 \text{ bar} \times 25 \text{ L}}{2 \text{ mol} \times 0.08314 \text{ bar L mol}^{-1} \text{ K}^{-1}}=2495.75 \text{ K}$$

$$P_3=0.664 \text{ bar} \quad V_3=25 \text{ L} \quad T_3=T_1$$

(Beware !! 1 bar·L = 100 J)

Process	1→2	2→3	3→1	For the Cycle
ΔU	$2C_{v,m}(T_2-T_1)$ = 99.62 kJ	$2C_{v,m}(T_3-T_2)$ = -99.62 kJ	0 (dT=0)	0 (state function)
ΔH	$2C_{p,m}(T_2-T_1)$ or $\Delta U+2R(T_2-T_1)$ = 139.468 kJ	$2C_{p,m}(T_3-T_2)$ or $\Delta U+2R(T_3-T_2)$ = -139.468 kJ	0 (dT=0)	0 (state function)
Q	$Q_p=\Delta H$ or $\Delta U-W$ = 139.468 kJ	$Q_v=\Delta U$ or $\Delta U-W$ = -99.62 kJ	=-W -5.35 kJ	34.498 kJ
W	$-P_1(V_2-V_1)$ = -39.84 J	0 (dv=0)	$-\int P dV = -2RT_1 \int \frac{dV}{V}$ $=-2RT \ln \frac{1}{25} = 5.35 \text{ kJ}$	-34.498 kJ

(b)

Same value as part (a), but different sign.

2.

Adiabatic $q=0$, expansion, $w<0$, $\Delta U = W < 0$, $\Delta H = C_p \Delta T < 0$
 $q=0$, $w < 0$, $\Delta U < 0$, $\Delta H < 0$

3.

Isothermal $\Delta T=0 \Rightarrow 0 = C_v \Delta T = C_p \Delta T$
 Expansion $w<0$, $q>0$
 $q>0$, $w < 0$, $\Delta U = 0$, $\Delta H = 0$

4. because $P_{ext}=0 \Rightarrow W=0$

adiabatic $q=0$

$\Rightarrow \Delta U = 0 \Rightarrow \Delta T=0 \Rightarrow \Delta H=0$

$q=0$, $w = 0$, $\Delta U = 0$, $\Delta H = 0$

5.

$$\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial P}{\partial V}\right)_T / \left(\frac{\partial T}{\partial V}\right)_P = \frac{-V}{-\kappa} / \frac{V}{\beta} = \frac{\beta}{\kappa}$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T \frac{\beta}{\kappa} - P$$

6.

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

$$dP = \frac{-\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial P}\right)_T} dT + \left(\frac{\partial P}{\partial V}\right)_T dV = \frac{\beta}{\kappa} dT - \frac{1}{\kappa V} dV$$

$$\Delta P = \frac{\beta}{\kappa} \Delta T + \frac{1}{\kappa} \int \frac{dV}{V} = \frac{\beta}{\kappa} \Delta T + \frac{1}{\kappa} \ln\left(\frac{V_f}{V_i}\right)$$

because $V_f = V_i + \Delta V$

and $V(T) = V_i + \left(\frac{dV}{dT}\right)_P (T - T_i) + H.O.T$

$\Rightarrow \Delta V \sim V_i \beta \Delta T$

$\Rightarrow \ln\left(\frac{V_f}{V_i}\right) = \ln(1 + \beta \Delta T)$

⊙ You can directly put the value $\beta \Delta T$ into logarithm

⊙ or using $\ln(1 + \beta \Delta T) \sim \beta \Delta T$ (because $\beta \Delta T \sim \frac{1}{100}$)

$$\Rightarrow \Delta P = \frac{(\beta_{\text{water}} - \beta_{\text{vessel}})}{\kappa} \Delta T = \frac{6.2 \cdot 10^{-5} K^{-1}}{4.59 \cdot 10^{-5} bar^{-1}} (82 - 13.56) = 92.44 \text{ bar}$$

⊙ never forget $P_f = P_i + \Delta P$

$$\Rightarrow \underline{P_f = 93.44 \text{ bar}}$$

7.

$$\left(\frac{\partial C_v}{\partial V} \right)_T = \left(\frac{\partial}{\partial T} \left(\frac{\partial P}{\partial T} \right)_V \right)_T = \left(\frac{\partial}{\partial T} \left(\frac{\partial U}{\partial V} \right)_T \right)_T$$

The order of differentiation can be reversed because U is a state function.

$$\text{Using the equation } \left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_V - P$$

$$\left(\frac{\partial C_v}{\partial V} \right)_T = \left(\frac{\partial}{\partial T} \left(T \left(\frac{\partial P}{\partial T} \right)_V - P \right) \right)_T = \left(\frac{\partial P}{\partial T} \right)_V + T \left(\frac{\partial^2 P}{\partial T^2} \right)_V - \left(\frac{\partial P}{\partial T} \right)_V = T \left(\frac{\partial^2 P}{\partial T^2} \right)_V$$

8.

(a)

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

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

(b)

$$\left(\frac{\partial \left(\frac{\partial P}{\partial T} \right)_V}{\partial V} \right)_T = \frac{-R}{(V_m - b)^2}$$

so dP is an exact differential.

$$\left(\frac{\partial \left(\frac{\partial P}{\partial V} \right)_T}{\partial T} \right)_V = \frac{-R}{(V_m - b)^2}$$

9.

$$\left(\frac{\partial T}{\partial P} \right)_H = - \left(\frac{\partial T}{\partial H} \right)_P / \left(\frac{\partial P}{\partial H} \right)_T = - \left(\frac{\partial H}{\partial P} \right)_T \frac{1}{C_p}$$

10.

(a)

Definition of the internal pressure:

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

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

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

$$T\left(\frac{\partial P}{\partial T}\right)_V - P = \frac{a}{V_m^2}$$

(b)

©At first, represent the μ_{JT} into a **calculable form**, (instead of $\frac{-(\frac{\partial T}{\partial P})_H}{C_p}$)

Because you have

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

$$\text{so} \left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{\partial U}{\partial P}\right)_T + \left(\frac{\partial PV}{\partial P}\right)_T$$

$$\text{and} \left(\frac{\partial U}{\partial P}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T$$

$$\left(\frac{\partial PV}{\partial P}\right)_T = P\left(\frac{\partial V}{\partial P}\right)_T + V$$

$$\begin{aligned} \Rightarrow \left(\frac{\partial H}{\partial P}\right)_T &= \left(\left(\frac{\partial U}{\partial V}\right)_T + P\right)\left(\frac{\partial V}{\partial P}\right)_T + V \\ &= \left(T\left(\frac{\partial P}{\partial T}\right)_V\right)\left(\frac{\partial V}{\partial P}\right)_T + V \\ &= V - T\left(\frac{\partial V}{\partial T}\right)_P \end{aligned}$$

©Second, you have to choose the **correct representations of V** or choose the **correct form of the fraction equation**.

©then solve the problem with same approximation

(You have the condition $P \sim 0$. In other words, $(1/V_m) \sim 0$ and you have $b < a < 1$)

*Method1:

Key point :Let V_m be calculable.

VDW E.O.S of gas can be represented by this form:

$$PV_m - bP + \frac{a}{V_m} - \frac{ab}{V_m^2} = RT$$

$\because a < 1$, and $ab \ll 1$

$\therefore \frac{ab}{V_m^2}$ is very small

$$PV_m \cong RT + bP - \frac{a}{V_m}$$

$$V_m \cong \frac{RT}{P} - \frac{a}{V_m P} + b \quad \text{and if we that } PV_m \sim RT$$

$$V_m \cong \frac{RT}{P} - \frac{a}{RT} + b \Rightarrow T \left(\frac{\partial V}{\partial T} \right)_P = \frac{RT}{P} + \frac{a}{RT}$$

$$\text{then we get } \left(\frac{\partial H}{\partial P} \right)_T \sim b - \frac{2a}{RT}$$

*Method2:

Key point :Similar to method1, but using the linear correction form of gas

$$Z = \frac{PV_m}{RT} = 1 + \frac{bP}{RT} - \frac{a}{V_m RT} + \frac{ab}{RTV_m^2}$$

to represent the form into the virial equation

$$\because \frac{ab}{RTV_m^2} \ll 1 \quad \text{and if we let } PV_m \sim RT \Rightarrow \frac{a}{V_m RT} = \frac{aP}{PV_m RT} \sim \frac{aP}{R^2 T^2}$$

$$Z \cong 1 + \left(b - \frac{a}{RT} \right) \frac{P}{RT} \quad (\text{actually, you can get Boyle Temperature} = \frac{a}{Rb} \text{ here})$$

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

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

$$\text{then } T \left(\frac{\partial V}{\partial T} \right)_P = \frac{RT}{P} + \frac{a}{RT} \Rightarrow \left(\frac{\partial H}{\partial P} \right)_T = b - \frac{2a}{RT}$$

* Method3: (highly recommended)

Key point :Find a clear solution of fraction

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

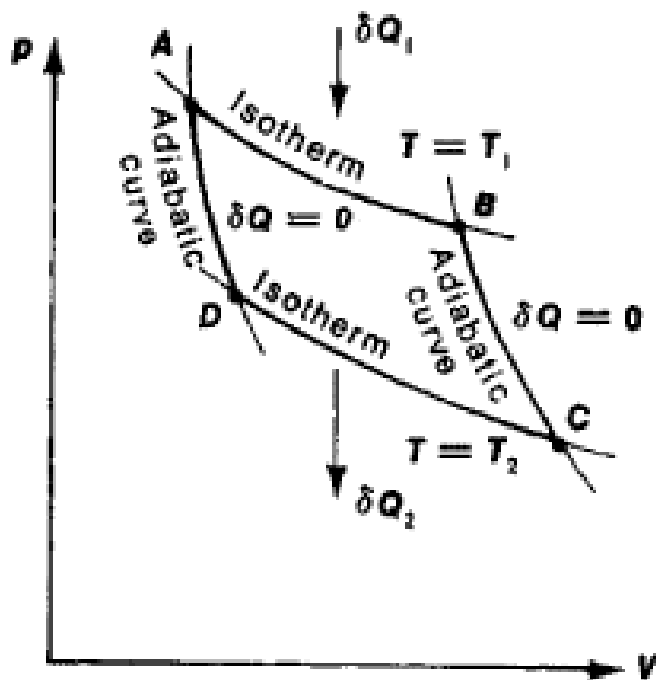
It's highly recommended to put V_m into the fraction before you do any further approximation.

$$\Rightarrow \frac{\frac{-V_m RT}{(V_m - b)^2} + \frac{2a}{V_m^2} + \frac{RT}{V_m - b}}{-\frac{RT}{(V_m - b)^2} + \frac{2a}{V_m^3}} = \frac{\frac{-bRT}{(V_m - b)^2} + \frac{2a}{V_m^2}}{-\frac{RT}{(V_m - b)^2} + \frac{2a}{V_m^3}} = \frac{\frac{b}{(V_m - b)^2} - \frac{2a}{V_m^2 RT}}{\frac{1}{(V_m - b)^2} - \frac{2a}{V_m^3 RT}}$$

$$\Rightarrow \frac{b - \frac{2a}{V_m^2 RT} (V_m - b)^2}{1 - \frac{2a}{V_m^3 RT} (V_m - b)^2} \approx b - \frac{2a}{V_m^2 RT} (V_m - b)^2 = b - \frac{2a}{RT} \left(1 - \frac{2b}{V_m} + \frac{b^2}{V_m^2} \right) \approx b - \frac{2a}{RT}$$

11.

(a)



(b)

In calculus, area inside the cycle is $\oint F_{(x)} dx$

here $F(x) \Rightarrow P, dx \Rightarrow dv$

so the area is the absolute value of works (because the value of area always > 0)

and $W_{\text{tot}} = W_{ab} + W_{bc} + W_{cd} + W_{da}$

$$W_{ab} = -nRT_H \ln\left(\frac{V_b}{V_a}\right)$$

$$W_{bc} = nC_V(T_C - T_H) \text{ and } T_H V_b^{\gamma-1} = T_C V_c^{\gamma-1}$$

$$W_{cd} = -nRT_C \ln\left(\frac{V_d}{V_c}\right)$$

$$W_{da} = nC_V(T_H - T_C) \text{ and } T_C V_d^{\gamma-1} = T_H V_a^{\gamma-1}$$

$$\frac{V_b}{V_a} = \frac{V_c}{V_d}$$

$$\Rightarrow W_{\text{tot}} = -nR(T_H - T_C) \ln\left(\frac{V_b}{V_a}\right) < 0$$

(c)

If we treat the carnot cycle as the heat pump

$$-Q_H = Q_C + W$$

$$\eta = \frac{-Q_H}{W} = \frac{nRT_H \ln\left(\frac{V_b}{V_a}\right)}{nR(T_H - T_C) \ln\left(\frac{V_b}{V_a}\right)} = \frac{T_H}{\Delta T}$$

$$\Rightarrow W = \Delta T \frac{-Q_H}{T_H}$$

(d)

$$\frac{q}{t} = C\Delta T$$

$$W_{\text{heatpump}} = \Delta T \frac{-Q_H}{T_H}$$

$$\Rightarrow \frac{W_{\text{heatpump}}}{t} = \frac{-C\Delta T^2}{T_H} \text{ and } \frac{W_{\text{direct heating}}}{t} = -C\Delta T$$

(Even if the heatpump is a reversible carnot heatpump, when $\frac{\Delta T}{T_H} > 1$,

it will be lower efficiency than direct heating)