

CHM225 - PROBLEM SET #1

Q1. Reversible isothermal compression
from state 1 (T_1, V_1) to 2 (T_2, V_2)

$$\Rightarrow T_2 = T_1$$

$$\text{equ. of state: } \frac{PV^2}{(V+c)} = RT$$

(a) work along this path

~~$$w = \int p(T) dV$$~~

$$w = \int -p dV$$

subst. the equ. of state

$$= - \int_{V_1}^{V_2} RT \frac{(V+c)}{V^2} dV$$

isothermal $\Rightarrow T$ is a const.

$$\omega = -RT_1 \int_{V_1}^{V_2} \left(\frac{1}{V} + \frac{c}{V^2} \right) dV$$

$$= -RT_1 \left(\ln\left(\frac{V_2}{V_1}\right) - c\left(\frac{1}{V_2} - \frac{1}{V_1}\right) \right)$$

$$\omega = RT_1 \ln\left(\frac{V_1}{V_2}\right) + cRT_1 \left(\frac{1}{V_2} - \frac{1}{V_1} \right)$$

(ii)

Calculate ΔU and q .

let $U = U(T, V)$

note: for a non-ideal gas U is a function of both T, V

$$\Rightarrow dU = \left(\frac{\partial U}{\partial V} \right)_T dV + \left(\frac{\partial U}{\partial T} \right)_V dT$$

for an isothermal process $dT = 0$

$$\Rightarrow dU = \left(\frac{\partial U}{\partial V} \right)_T dV$$

from problem #3 $\left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_V - P$

$$P = RT \left(\frac{1}{V} + \frac{c}{V^2} \right)$$

$$\Rightarrow \left(\frac{\partial P}{\partial T} \right)_V = R \left(\frac{1}{V} + \frac{c}{V^2} \right) = \frac{P}{T}$$

$$\Rightarrow \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{P}{T}\right) - P = 0$$

So U is a function of T only

$$U = U(T)$$

since temperature is constant.

$$\Delta U = U(T_2) - U(T_1) = U(T) - U(T) = 0$$

there is no change in internal energy.

Using the 1st law of thermodynamics.

$$q = \Delta U - w$$

$$q = -w$$

$$q = -RT \ln\left(\frac{V_1}{V_2}\right) - cRT\left(\frac{1}{V_2} - \frac{1}{V_1}\right)$$

(iii) Irreversible compression at pressure P_2 .

$$\begin{aligned} w_{\text{irrev}} &= - \int_{V_1}^{V_2} P_{\text{ext}} dV \\ &= - P_2 (V_2 - V_1) \end{aligned}$$

the pressure P_2 can be related to T_1 and V_2 by the eqn of state: $P_2 = \frac{RT_1(V_2 + c)}{V_2^2}$

$$w_{\text{irrev}} = - \frac{RT_1 (V_2 + c)(V_2 - V_1)}{V_2^2} = -RT_1 \left[1 - \frac{V_1}{V_2} + c \left(\frac{1}{V_2} - \frac{1}{V_2^2} \right) \right]$$

$$w_{\text{irrev}} = -RT_1 \left[1 - \frac{V_1}{V_2} - c \frac{V_1}{V_2} \left(\frac{1}{V_2} - \frac{1}{V_1} \right) \right] > w_{\text{rev}} \quad (c > 0)$$

1(iv) We obtain the ideal gas equation in the limit that $c \rightarrow 0$, i.e.

$$\frac{PV^2}{(V+c)} = RT \xrightarrow{c=0} PV = RT$$

\Rightarrow work done on ideal gas during isothermal compression.

$$\begin{aligned} w_{\text{ideal}} &= \lim_{c \rightarrow 0} w_{\text{nonideal}} \\ &= \lim_{c \rightarrow 0} \left[RT_1 \ln\left(\frac{V_1}{V_2}\right) - RT_1 c \left(\frac{1}{V_2} - \frac{1}{V_1}\right) \right] \end{aligned}$$

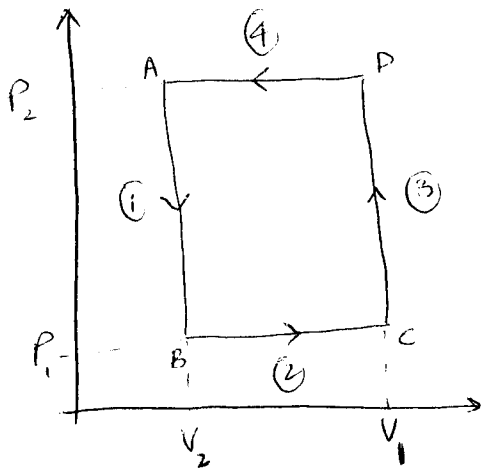
$$w_{\text{ideal}} = RT_1 \ln\left(\frac{V_1}{V_2}\right)$$

$$\Rightarrow w_{\text{ideal}} - w_{\text{nonideal}} = +RT_1 c \left(\frac{1}{V_2} - \frac{1}{V_1}\right) > 0$$

for compression $V_2 < V_1$ (assuming $c > 0$)

$$\begin{aligned} \Rightarrow & \boxed{w_{\text{ideal}} > w_{\text{non-ideal}} \quad (c > 0)} \\ & \boxed{w_{\text{ideal}} < w_{\text{non-ideal}} \quad (c < 0)} \end{aligned}$$

Q2.



(i) compute work in each step.

$$\boxed{\begin{matrix} w_{(1)} = 0 \\ w_{(3)} = 0 \end{matrix}} \quad (\text{const. } V \text{ process})$$

$$w_{(2)} = - \int_{V_2}^{V_1} P_1 dV$$

$$\boxed{w_{(2)} = P_1 (V_2 - V_1)} \quad (\text{const. pressure process})$$

$$w_{(4)} = - \int_{V_1}^{V_2} P_2 dV$$

$$\boxed{w_{(4)} = -P_2 (V_2 - V_1)} \quad (\text{const. pressure process})$$

(ii) $\boxed{\Delta U_{\text{cycle}} = 0}$ (U is a state variable)

$$w_{\text{cycle}} = \sum_{i=1}^4 w_{(i)} = P_1 (V_2 - V_1) - P_2 (V_2 - V_1)$$

$$\boxed{w_{\text{cycle}} = -(P_2 - P_1)(V_2 - V_1)}$$

$$q_{\text{cycle}} = \Delta U_{\text{cycle}} - w_{\text{cycle}}$$

$$= -w_{\text{cycle}}$$

$$q_{\text{cycle}} = \boxed{(p_2 - p_1)(V_2 - V_1)}$$

(iii)

$$\boxed{\Delta U_{\text{cycle}}^{\text{rev}} = 0}$$

$\Delta w_{\text{cycle}}^{\text{rev}} = -w_{\text{cycle}}$ (all limits of integration)
are interchanged

$$\boxed{w_{\text{cycle}}^{\text{rev}} = (p_2 - p_1)(V_2 - V_1)}$$

$$q_{\text{cycle}}^{\text{rev}} = \Delta U_{\text{cycle}}^{\text{rev}} - w_{\text{cycle}}^{\text{rev}}$$

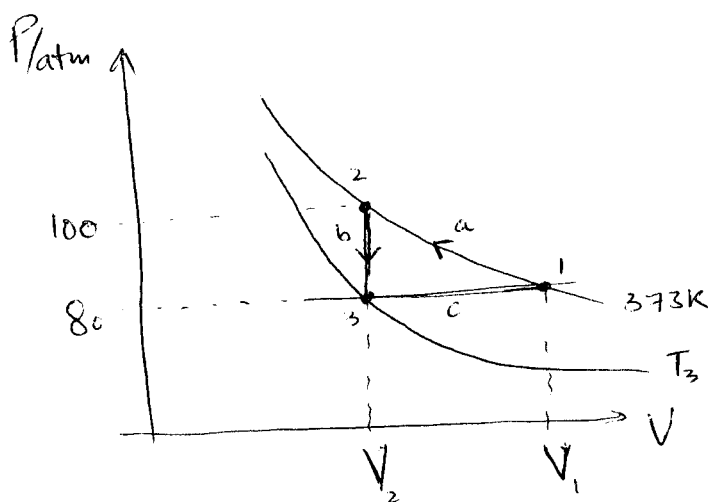
$$\boxed{q_{\text{cycle}}^{\text{rev}} = -(p_2 - p_1)(V_2 - V_1)}$$

Q3. Consider 1 mole of CO_2 gas which obey:
 the VdW eqn of state: ~~is not~~

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

P in atm
 V in L
 T in K

$$a = 3.592 \frac{\text{L}^2 \cdot \text{atm}}{\text{mol}^2}; \quad b = 0.09265 \frac{\text{L}}{\text{mol}}$$



- a: isothermal process
- b: isochoric process
- c: isobaric process.

We first calculate V_1 and V_2 .

write eqn of state as:

$$PV^3 - (bp + RT)V^2 + aV - ab = 0$$

Subst $P = P_1 = 80 \text{ atm}$

$$T = T_1 = 373 \text{ K}$$

solve the cubic eqn (eg. using Matlab)

$$V_1 = 0.295 \text{ L (only real sol}^n\text{)}$$

similarly we can solve for V_2

Subst $P = P_2 = 100 \text{ atm}$

$$T = T_1 = 373 \text{ K}$$

$$\Rightarrow V_2 = 0.215 \text{ L}$$

Calculate $\Delta U_a = \int_1^2 dU$

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

since a is an isothermal process, therefore

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV$$

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

$$P = \frac{RT}{V-b} - \frac{a}{V^2} \quad (\text{vdW eqn of state})$$

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

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

$$= \frac{RT}{V-b} - \left[\frac{RT}{V-b} - \frac{a}{V^2} \right] = \frac{a}{V^2}$$

$$\Rightarrow \Delta U_a = \int_1^2 dU = \int_{V_1}^{V_2} \left(\frac{\partial U}{\partial V} \right)_T dV$$

$$\Delta U_a = \int_{V_1}^{V_2} \frac{a}{V^2} dV = \left[\frac{a}{V_1} - \frac{a}{V_2} \right]$$

$$\Rightarrow \Delta U_a = -4.531$$

1st Law of Thermodynamics states:

$$\Delta U_a = q_a + w_a$$

$$w_a = - \int_1^2 P dV = - \int \left[\frac{RT}{V-b} - \frac{a}{V^2} \right] dV$$

$$w_a = RT_1 \ln \left(\frac{V_2-b}{V_1-b} \right) + \left(\frac{a}{V_1} - \frac{a}{V_2} \right)$$

$$= 11.671 - 4.531 =$$

$$w_a = 7.140$$

$$\Rightarrow q_a = \Delta U_a - w_a = a \left[\frac{1}{V_1} - \frac{1}{V_2} \right] - RT_1 \ln \left(\frac{V_2-b}{V_1-b} \right) - a \left[\frac{1}{V_1} - \frac{1}{V_2} \right]$$

$$q_a = RT_1 \ln \left(\frac{V_2-b}{V_1-b} \right) = -11.671$$

For process b. 2 \rightarrow 3 we need to determine T_3

Using vdW eqn of state with

$$P = P_3 = 80 \text{ atm}$$

$$V = V_3 = V_2 = 0.215 \text{ L}$$

we get $T_3 = 331.23 \text{ K}$

Calculate w_b , q_b and ΔU_b .

$$\boxed{w_b = 0} \text{ (isochoric process)}$$

$$\Delta U_b = \int_2^3 dU_b$$

$$dU = \left(\frac{\partial U}{\partial V} \right)_T dV + \left(\frac{\partial U}{\partial T} \right)_V dT = C_V dT$$

$$\Rightarrow \Delta U_b = \int_{T_2}^{T_3} C_V dT = C_V (T_3 - T_2)$$

$$\boxed{\Delta U_b = \frac{3R}{2} (T_3 - T_2)}$$
$$\Delta U_b = -5.141$$

$$\boxed{q_b = \Delta U_b - w_b = \Delta U_b = \frac{3R}{2} (T_3 - T_2)}$$
$$q_b = -5.141$$

Consider process c: 3 → 1

$$\begin{aligned}w_c &= - \int P_c dV \\ &= - P_3 \int_{V_3}^{V_1} dV\end{aligned}$$

$$\begin{aligned}w_c &= - P_3 (V_1 - V_3) \\ w_c &= - 6.40\end{aligned}$$

Since U is a state fn.

$$\Delta U_{\text{cycle}} = 0$$

$$\Rightarrow \Delta U_a + \Delta U_b + \Delta U_c = 0$$

$$\Rightarrow \Delta U_c = -\Delta U_a - \Delta U_b$$

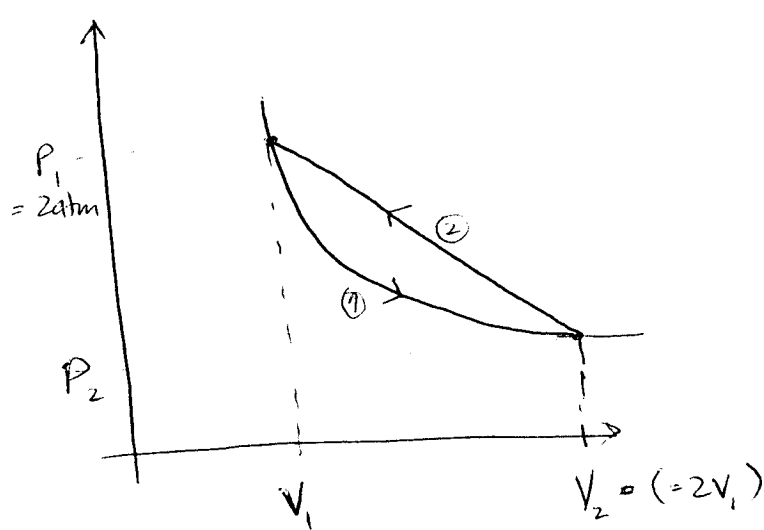
$$= -a \left[\frac{1}{V_1} - \frac{1}{V_2} \right] - \frac{3R}{2} (T_3 - T_2)$$

$$\begin{aligned}\Delta U_c &= a \left[\frac{1}{V_2} - \frac{1}{V_1} \right] + \frac{3R}{2} (T_2 - T_3) \\ \Rightarrow \Delta U_c &= 9.672\end{aligned}$$

$$\Rightarrow q_c = \Delta U_c - w_c$$

$$\begin{aligned}q_c &= a \left[\frac{1}{V_2} - \frac{1}{V_1} \right] + \frac{3R}{2} (T_2 - T_3) + P_3 [V_1 - V_3] \\ q_c &= 16.072\end{aligned}$$

Q4.



Process 1: reversible adiabatic expansion.

for an adiabatic process ①: $P_1 V_1^\gamma = P_2 V_2^\gamma$

where $\gamma = \frac{C_p}{C_v} = \frac{5}{3}$ (monatomic ideal gas)

the eqn of state: $PV = RT$ (for 1 mol).

$$P_2 = P_1 \left(\frac{V_1}{V_2} \right)^\gamma = 2 \left(\frac{V_1}{2V_1} \right)^{5/3} = 2^{-2/3} \text{ atm.}$$

$$T_1 = \frac{P_1 V_1}{R} = \frac{2V_1}{R}$$

$$T_2 = \frac{P_2 V_2}{R} = \frac{2^{-2/3} \cdot 2V_1}{R} = \frac{2^{1/3} V_1}{R}$$

$$\Delta U_{(1)} = C_v(T_2 - T_1)$$

$$= \frac{3}{2}R \left(\frac{2^{1/3}V_1}{R} - \frac{2V_1}{R} \right)$$

$$\Delta U_{(1)} = 3V_1(2^{-2/3} - 1)$$

$$Q_{(1)} = 0 \quad (\text{adiabatic process})$$

$$W_{(1)} = \Delta U_{(1)}$$

(1st law of Thermodynamics)

For process (2) along a straight line:
since U is a state fn.

$$\Delta U_{(2)} = -\Delta U_{(1)}$$

$$W_{(2)} = -\int_{V_2}^{V_1} P dV$$

= Area under the straight line
between $V = V_1$ to $V = V_2$.

$$W_{(2)} = \frac{(P_1 + P_2)(V_2 - V_1)}{2}$$

[area of trapezoid
= $\frac{\text{sum of // sides}}{2} \times \perp \text{ height}$]

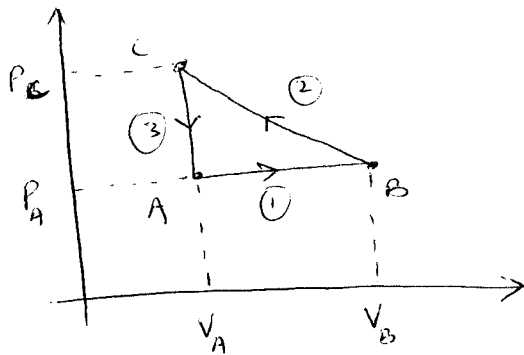
$$= \frac{(2 + 2^{-2/3})}{2} (2V_1 - V_1)$$

$$W_{(2)} = (1 + 2^{-5/3})V_1$$

$$Q_{(2)} = \Delta U_{(2)} - W_{(2)} = 3V_1(2^{-2/3} - 1) - (1 + 2^{-5/3})V_1$$

$$Q_{(2)} = V_1(3 \cdot 2^{-2/3} - 4 - 2^{-5/3})$$

$$U = \frac{5}{2} PV + C$$



(i) Calculate q & w for each step.

$$\Delta U_{\text{①}} = U_B - U_A = \left(\frac{5}{2} P_B V_B + C \right) - \left(\frac{5}{2} P_A V_A + C \right)$$

$$\Delta U_{\text{①}} = \frac{5}{2} P_A (V_B - V_A)$$

Since $P_B = P_A$

$$w_{\text{①}} = - \int p dV = - P_A \int_{V_A}^{V_B} dV$$

$$w_{\text{①}} = - P_A (V_B - V_A)$$

$$q_{\text{①}} = \Delta U_{\text{①}} - w_{\text{①}}$$

$$= \left[\frac{5}{2} P_A (V_B - V_A) \right] - \left[- P_A (V_B - V_A) \right]$$

$$= (V_B - V_A) \left(\frac{5}{2} P_A + P_A \right)$$

$$q_{\text{①}} = \frac{7}{2} P_A (V_B - V_A)$$

$$\Delta U_{(2)} = U_c - U_b = \left(\frac{5}{2} P_c V_c + K \right) - \left(\frac{5}{2} P_b V_b + K \right)$$

$$= \frac{5}{2} V_A \left(\frac{P_c}{P_A} - \frac{P_b}{P_A} \right) \quad \text{since } V_c = V_A$$

$$P_b = P_A$$

$$\Delta U_{(2)} = \frac{5}{2} (P_c V_A - P_A V_B)$$

$$w_{(2)} = - \int_{V_B}^{V_c} P_{(2)} dV = \text{Area under the straight line between } V = V_c \text{ to } V = V_B$$

$$= - \frac{(P_b + P_c)(V_c - V_B)}{2}$$

$$w_{(2)} = - \frac{(P_A + P_c)(V_A - V_B)}{2}$$

$$q_{(2)} = \Delta U_{(2)} - w_{(2)}$$

$$= \left[\frac{5}{2} V_A \left(\frac{P_c}{P_A} - \frac{P_b}{P_A} \right) \right] - \left[- \frac{(P_A + P_c)(V_A - V_B)}{2} \right]$$

$$= \left[\frac{5}{2} (P_c V_A - P_A V_B) \right] - \left[- \frac{(P_A + P_c)(V_A - V_B)}{2} \right]$$

$$q_{(2)} = 3(P_c V_A - P_A V_B) + \frac{1}{2}(P_A V_A - P_c V_B)$$

$$\Delta U_{(3)} = U_A - U_c = \left[\frac{5}{2} (P_A V_A + K) \right] - \left[\frac{5}{2} P_c V_c + K \right]$$

$$\Delta U_{(3)} = \frac{5}{2} V_A (P_A - P_c)$$

(isochoric process)

$$w_{(3)} = 0$$

$$q_{(3)} = \Delta U_{(3)} - w_{(3)} = \Delta U_{(3)} = \frac{5}{2} V_A (P_A - P_c)$$

S(ii) parabolic path from A to B.

$$P = P_A + C_2 \left[V^2 - V(V_A + V_B) + V_A V_B \right]$$

$$\Delta U = \Delta U_{(1)} \quad (\text{since } U \text{ is a state fn.})$$

$\Delta U \text{ is path independent}$

$$= \int_{V_A}^{V_B} P_A (V_B - V_A)$$

$$W = - \int_{V_A}^{V_B} P dV = - \int_{V_A}^{V_B} \left(P_A + C_2 \left[V^2 - V(V_A + V_B) + V_A V_B \right] \right) dV$$

$$= -P_A (V_B - V_A) - C_2 \left[\frac{V^3}{3} - \frac{V^2(V_A + V_B)}{2} + V V_A V_B \right]_{V_A}^{V_B}$$

$$= -P_A (V_B - V_A) - C_2 \left[\frac{V_B^3 - V_A^3}{3} + \frac{V_B^2 - V_A^2}{2} (V_A + V_B) - (V_B - V_A) V_A V_B \right]$$

$$= (V_B - V_A) \left[-P_A + C_2 \left(\frac{-V_B^2 - V_A V_B - V_A^2}{3} + \frac{(V_B + V_A)^2}{2} V_A V_B \right) \right]$$

$$= (V_B - V_A) \left[-P_A + \frac{C_2}{6} \left(-2V_B^2 - 2V_A V_B - V_A^2 + 3V_B^2 + 6V_A V_B + 3V_A^2 - 6V_A V_B \right) \right]$$

$$= (V_B - V_A) \left[-P_A + \frac{C_2}{6} (V_A^2 - 2V_A V_B + V_B^2) \right]$$

$$= (V_B - V_A) \left[-P_A + \frac{C_2}{6} (V_B - V_A)^2 \right]$$

$$W = -P_A (V_B - V_A) + \frac{C_2}{6} (V_B - V_A)^3$$

$$q = \Delta U - w$$

$$= \left[\frac{5}{2} P_A (V_B - V_A) \right] - \left[-P_A (V_B - V_A) + \frac{C_2}{6} (V_B - V_A)^3 \right]$$

$$q = \frac{7}{2} P_A (V_B - V_A) - \frac{C_2}{6} (V_B - V_A)^3$$

(iii)

find $P = P(V)$ along which $dq = 0$.

First law: $dU = \delta q + \delta w$

$$dU = \delta w = -pdV \quad \text{--- (1)}$$

~~Eqn of state~~

Gas obeys: $U = \frac{5}{2} PV + C$

$$\Rightarrow dU = \frac{5}{2} (pdV + Vdp) \quad \text{--- (2)}$$

equating (1) & (2)

$$\frac{5}{2} pdV + \frac{5}{2} Vdp = -pdV$$

$$\Rightarrow \frac{7}{2} pdV = -\frac{5}{2} Vdp$$

$$\Rightarrow \frac{dp}{p} = -\frac{7}{5} \frac{dV}{V} \quad (\text{integrate}).$$

$$\Rightarrow PV^{7/5} = \text{constant.}$$

$$\Rightarrow \boxed{P = kV^{-7/5}} \quad (\text{where } k \text{ is an arbitrary constant}).$$