

1. The figure alongside shows two isothermal reversible lines for 1 kmol of a diatomic ideal gas ($C_p = 7R/2$). State 1 and two are defined as follows :

	State 1	State 2
P, atm	1	3
V, m ³	22.42	8.28
T, K	273.15	303.00

(a) Traverse from state 1 to 2 by the following routes :

Route I : (i) Isothermal process state 1' followed by (II) a constant volume process, all reversible.

Route II : (ii) An adiabatic process to state 3 followed by (ii) an isobaric process, all reversible.

(b) Route III : Now return from state 2 to state 1 along a straight line in the P-V diagram.

For each of the sub-processes calculate w, q, ΔE , ΔH , and $\int \frac{\delta q}{T}$, and complete the table.

10 marks

What are your observations on the values in the shaded rows ?

2 marks

initial		1	22.42	273.15
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Process		Final			q kJ	w kJ	ΔE kJ	ΔH kJ	$\int_i^f \frac{\delta q_{rev}}{T}$ kJ/K
		P Atm	V m ³	T K					
Route I	(i)	2.704	8.289	273.15	-2259.0	-2259.0	0	0	-8.270
	(ii)	3	8.289	303.00	620.43	0	620.43	868.6	+2.156
	total				-1638.57	-2259.0	620.43	868.6	-6.114
Route II	(i)	3	10.229	373.88	0	-2093.6	2093.6	2931.0	0
	(ii)	3	8.289	303	-2062.42	-589.27	-1473.15	-2062.42	-6.117
	total				-2062.42	-2682.87	620.45	868.58	-6.117
Route III		1	22.42	273.15	2242.51	2862.94	-620.43	-868.61	6.12
Route I + III					603.94	603.94	0	0	0
Route II + III					180.09	180.07	0	0	0

Comment on the shaded rows.

1. q and w are different for Route I and Route II.
2. q and w are different for the two cycles
3. ΔE , ΔH and $\int \frac{\delta q_{rev}}{T}$ are identical for Route I and Route II (except round-off error)
4. ΔE , ΔH and $\int \frac{\delta q_{rev}}{T}$ are zero for the two cyclic processes.
5. $\int \frac{\delta q_{rev}}{T}$ seems to be a state property.

Calculations:

Route I: (i) $q = w = 1 \times 8.314 \times 273.15 \times \ln\left(\frac{1}{2.704}\right) = -2259.0$ } Isothermal
 $\Delta E = \Delta H = 0$; $\int \frac{\delta q}{T} = \frac{q}{T} = \frac{-2259.0}{273.15} = -8.270$ }

(ii) $w = 0$, $\Delta E = \int n C_v dT = \frac{5}{2} \times 8.314 \times (303 - 273.15) = 620.43$

$\Delta E = 620.43$; $\Delta H = \Delta E + \Delta(PV) = 620.43 + \frac{(3 \times 8.289 - 1 \times 22.42) \times 10^5}{1000}$

$= q_v$
 $\int \frac{\delta q_{rev}}{T} = \int C_v d \ln T = \frac{5}{2} \times 8.314 \times \ln\left(\frac{303}{273.15}\right) = 2.156 \text{ kJ/K}$

Route II: (i) Since the second part is isobaric, the final pr. is 3 atm

$P_1 V_1^\gamma = P_3 V_3^\gamma$; $V_3 = \left(\frac{P_1}{P_3}\right)^{\frac{1}{\gamma}} V_1 = \left(\frac{1}{3}\right)^{\frac{1}{1.4}} \cdot 22.42 = 10.229 \text{ m}^3$
 $T_3 = 373.88 \text{ K}$

$q_f = 0$; $w = \frac{P_1 V_1 - P_3 V_3}{\gamma - 1} = -2093.6 \text{ kJ}$

$\Delta E = 2093.6 \text{ kJ}$; $\Delta H = 2093.6 + \Delta PV = 2093.6 + 837.44 = 2931.0$

Check $\Delta H = C_p \Delta T = 2931.04$

$\int \frac{\delta q_{rev}}{T} = 0$

(ii) Isobaric compression to 8.289 m^3 & 303 K .

$\Delta E = C_v \Delta T = \frac{5}{2} R (303 - 373.88) = -1473.15$

$\Delta H = C_p \Delta T = \frac{7}{2} R (303 - 373.88) = -2062.42 = q_p$

$w = q_p - \Delta E = -2062.42 + 1473.15 = -589.27$

Verify $w = P \Delta V = 3 \times \frac{1.013 \times 10^5}{1000} (8.289 - 10.229)$

$\int \frac{\delta q}{T} = \int C_p \frac{dT}{T} = C_p \ln \frac{T_2}{T_1} = \frac{7}{2} \times 8.314 \times \ln \frac{303}{373.88} = -6.117$

Route III:

$\Delta E = C_v \Delta T = -620.43$; $\Delta H = 868.61$

$w = \text{area under the curve} = \frac{(P_1 + P_2)}{2} \cdot \Delta V = \frac{2 \times 1.012 \times 10^5}{2} \times \Delta V$

$= 2 \times 1.012 \times 10^2 (22.42 - 8.289)$
 $= 2862.94$

$q = \Delta E + w = 2862.94 - 620.43 = 2242.51$

2. A fuel gas at 298K [50:50 (by volume) mixture of methane and propane (C_3H_8)] is burnt in a burner with 10 % excess air at 298K ($O_2:N_2=21:79$, and 5 vol% moisture) . Calculate the adiabatic flame temperature. Present your results as mass and heat balance tables. Complete the heat balance table after calculating the flame temperature and verify your results. **Take one kmol of fuel gas as the basis.**
(Only tables will be corrected. Without the completed tables, the answer may not be corrected). **8 marks**

2.

Mass balance : Basis 1 kmol fuel gas					
input	kmoles	kg	Output	kmoles	kg
CH ₄	0.5	8.0	CO ₂	2.000	88.00
C ₃ H ₈	0.5	22.10	H ₂ O	3.9649	71.37
O ₂	3.850	123.20	N ₂	14.483	405.52
N ₂	14.483	405.52	O ₂	0.350	11.20
H ₂ O	0.9649	17.37			
Total		576.07	Total		576.07

Heat Balance : Basis : ^{Zero} all materials at 298 K have sensible heat			
Input	kJ	Output	kJ
Sensible heats		Sensible heats	
CH ₄	0	CO ₂ : $2(61.0T_f - 36500) = 122T_f - 61000$	199817
C ₃ H ₈	0	H ₂ O : $3.9649(47.4T_f - 22200) = 187.94T_f - 88021$	313765
O ₂	0	N ₂ : $14.483(36.4T_f - 16500) = 527.18T_f - 238970$	888056
N ₂	0	O ₂ : $0.35(36.2T_f - 13500) = 12.67T_f - 4725$	22212
H ₂ O		Losses	0
Reaction heat ($-\sum n_i \Delta H_i$) = $0.5(803000 + 2045000)$	1424000		
Total	1424000	Total	1423850

$$T_f (122 + 187.9 + 527.18 + 12.6) - (61000 + 88021 + 238970 + 4725) = 1424000$$

$$T_f = \frac{1}{849.79} (1424000 + 392716) = \underline{\underline{2137.84 K}}$$

OK

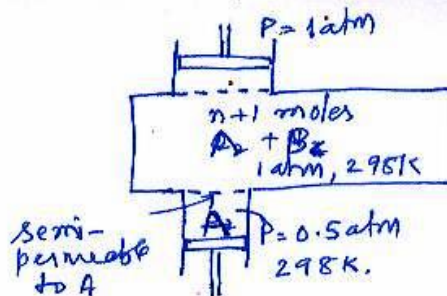
3. Two ideal gases A and B, 0.5 moles each, and at 300K and 1 atm. pressure, are initially kept in two chambers, separated by an impermeable wall. The wall separating them is then removed and the gases are allowed to mix, till you get a homogeneous mixture. Devise a reversible process to separate the gases and restore them to the original state. After the separation process what is the net effect on the surrounding ?

[Hint : Across a semi-permeable membrane permitting one of the gases to go through, the partial pressures of that gas are equal at equilibrium.]

5 marks

- Mix the 1 mole 50:50 mixture with say n moles of a similar mixture.

No w , no q .



- Connect two piston/cylinder systems as shown. One of them is separated from the chamber with a semi-permeable membrane for ~~oxygen~~ ^A.
- Across the membrane: 1 atm 298K on the mixture side
0.5 atm 298K on the pure ~~oxygen~~ ^A side.
- Move the pistons: reversibly, and extract 0.5 mol. ~~oxygen~~ ^A at 0.5 atm & 298K.

No q ; $w = \Delta(PV) = 0$. (confirm)

- similarly remove 0.5 mol ~~oxygen~~ ^B at 0.5 atm & 298K.
- you leave n moles of mixture that you have borrowed as you borrowed it.

AND: ~~oxygen~~ ^A & B separated, at 298K, but at 0.5 atm.
No q & no w .

- Compress the two gases isothermally to 1 atm. You have reached the original state.

$$w_{\text{sys}} = -2 \times \left(0.5 RT \ln \frac{1}{0.5} \right) = -RT \ln 2 = q_{\text{sys}} = -1717.3 \text{ J}$$

Surrounding loses much energy & gains int. energy } = 1717.3 J