

1. (15%) 2.25 moles of an ideal gas with $C_{v,m} = 3/2 R$ undergoes the transformations described in the following list from an initial state described by $T = 310.K$. and $P = 1.00$ bar. Calculate q , w , ΔU , ΔH , and ΔS for each process.

- The gas is heated to 675 K at a constant external pressure of 1.00 bar.
- The gas is heated to 675 K at a constant volume corresponding to the initial volume.
- The gas undergoes a reversible isothermal expansion at 310.K until the pressure is one third of its initial value.

Soln.

- The gas is heated to 675 K at a constant pressure of 1.00 bar.

$$V_i = \frac{nRT_i}{P_i} = \frac{2.25\text{mol} \times 8.314\text{Jmol}^{-1}\text{K}^{-1} \times 310\text{K}}{10^5\text{Pa}} = 5.80 \times 10^{-2}\text{m}^3$$

$$V_f = \frac{T_f}{T_i} V_i = \frac{675\text{K}}{310\text{K}} \times 5.80 \times 10^{-2}\text{m}^3 = 0.126\text{m}^3$$

$$w = -P_{\text{external}}\Delta V = -10^5\text{Pa} \times (0.126\text{m}^3 - 5.80 \times 10^{-2}\text{m}^3) = -6.83 \times 10^3\text{J}$$

$$\Delta U = nC_{v,m}\Delta T = 2.25\text{mol} \times \frac{3 \times 8.314\text{Jmol}^{-1}\text{K}^{-1}}{2} \times 365\text{K} = 10.2 \times 10^3\text{J}$$

$$q = \Delta H = \Delta U - w = 10.2 \times 10^3\text{J} + 6.83 \times 10^3\text{J} = 17.1 \times 10^3\text{J}$$

$$\Delta S = nC_{p,m}\ln\frac{T_f}{T_i} = 2.25\text{mol} \times \left(\frac{3}{2} + 1\right) \times 8.314\text{Jmol}^{-1}\text{K}^{-1} \ln\frac{675\text{K}}{310\text{K}} = 36.4\text{JK}^{-1}$$

- The gas is heated to 675K at a constant volume corresponding to the initial volume. $w=0$ because $\Delta V=0$.

$$\begin{aligned}\Delta U = q &= nC_{v,m}\Delta T = 2.25\text{mol} \times \frac{3 \times 8.314\text{J mol}^{-1}\text{K}^{-1}}{2} \times 365\text{K} \\ &= 10.2 \times 10^3\text{J}\end{aligned}$$

$$\Delta H = nC_{p,m}\Delta T = 2.25\text{mol} \times \frac{5 \times 8.314\text{J mol}^{-1}\text{K}^{-1}}{2} \times 365\text{K} = 17.1 \times 10^3\text{J}$$

$$\Delta S = nC_{v,m}\ln\frac{T_f}{T_i} = 2.25\text{mol} \times \left(\frac{3}{2}\right) \times 8.314\text{Jmol}^{-1}\text{K}^{-1} \ln\frac{675\text{K}}{310\text{K}} = 21.8\text{JK}^{-1}$$

- The gas undergoes a reversible isothermal expansion at 310K until the pressure is one third of its initial value. $\Delta U = \Delta H = 0$ because $\Delta T = 0$

$$\begin{aligned}w_{\text{reversible}} &= -q = -nRT\ln\frac{V_f}{V_i} = -2.25\text{mol} \times 8.314\text{Jmol}^{-1}\text{K}^{-1} \times 310\text{K} \times \ln 3 \\ &= -6.37 \times 10^3\text{J}\end{aligned}$$

$$\begin{aligned}
\Delta S &= -nR \ln \frac{P_f}{P_i} + nC_p \ln \frac{T_f}{T_i} \\
&= -2.25 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times \ln \frac{1}{3} + 2.25 \text{ mol} \times \left(\frac{5}{2}\right) \times 8.314 \text{ J mol}^{-1} \ln 1 \\
&= 20.6 \text{ J K}^{-1}
\end{aligned}$$

2. (15%) Consider the reversible Carnot cycle with 1.25 mol of an ideal gas with $C_{V,m} = 5/2 R$ as the working substance. The initial isothermal expansion occurs at the hot reservoir temperature of $T_{hot} = 740. \text{ K}$ from an initial volume of 3.75 (V_a) to a volume of 12.8 L (V_b). The system then undergoes an adiabatic expansion until the temperature falls to $T_{cold} = 310. \text{ K}$. The system then undergoes an isothermal compression and a subsequent adiabatic compression until the initial state described by $T_a = 740. \text{ K}$ and $V_a = 3.75 \text{ L}$ is reached.

- Calculate V_c and V_d .
- Calculate w for each step in the cycle and for the total cycle.
- Calculate ε and the amount of heat that is extracted from the hot reservoir to do 1.00 kJ of work in the surroundings.

Soln.

- Calculate V_c and V_d

$$V_c = V_b \left(\frac{T_c}{T_b}\right)^{\frac{1}{1-\gamma}} = 12.8 \text{ L} \times \left(\frac{310. \text{ K}}{740. \text{ K}}\right)^{\frac{1}{1-1.4}} = 113 \text{ L}$$

$$V_d = V_a \left(\frac{T_d}{T_a}\right)^{\frac{1}{1-\gamma}} = 3.75 \text{ L} \times \left(\frac{310. \text{ K}}{740. \text{ K}}\right)^{\frac{1}{1-1.4}} = 33.0 \text{ L}$$

- Calculate w for each step in the cycle and for the total cycle.

$$\begin{aligned}
w_{ab} &= -nRT_a \ln \frac{V_b}{V_a} = 1.25 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times \ln \frac{12.8 \text{ L}}{3.75 \text{ L}} \\
&= -9.44 \times 10^3 \text{ J}
\end{aligned}$$

$$\begin{aligned}
w_{bc} &= nC_{V,m}(T_c - T_b) \\
&= 1.25 \text{ mol} \times 2.5 \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times (310. \text{ K} - 740. \text{ K}) \\
&= -11.2 \times 10^3 \text{ J}
\end{aligned}$$

$$\begin{aligned}
w_{cd} &= -nRT_a \ln \frac{V_d}{V_c} = 1.25 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times \ln \frac{33.0 \text{ L}}{113 \text{ L}} \\
&= 3.96 \times 10^3 \text{ J}
\end{aligned}$$

$$\begin{aligned}
w_{da} &= nC_{V,m}(T_a - T_d) \\
&= 1.75\text{mol} \times \frac{5}{2} \times 8.314\text{Jmol}^{-1}\text{K}^{-1} \times (740.\text{K} - 310.\text{K}) \\
&= +11.2 \times 10^3\text{J} \\
w_{total} &= -9.44 \times 10^3\text{J} - 11.2 \times 10^3\text{J} + 3.96 \times 10^3\text{J} + 11.2 \times 10^3\text{J} \\
&= -5.49 \times 10^3\text{J}
\end{aligned}$$

- c. Calculate ε and the amount of heat that is extracted from the hot reservoir to do 1.00 kJ of work in the surroundings.

$$\varepsilon = 1 - \frac{T_{cold}}{T_{hot}} = 1 - \frac{310.\text{K}}{740.\text{K}} = 0.581 \quad q = \frac{w}{\varepsilon} = \frac{1.00 \times 10^3\text{J}}{0.581} = 1.72 \times 10^3\text{J}$$

3.(15%) 3 mole of an ideal gas with $C_{V,m} = 3/2 R$ undergoes the transformations described in the following list. (Initial state $T = 298\text{ K}$ and $P = 4.5\text{ bar}$.)

Calculate q , w , ΔU , ΔH , and ΔS for each process.

- The gas undergoes a reversible adiabatic expansion until the final pressure is one third its initial value.
- The gas undergoes an adiabatic expansion against a constant external pressure of 1.50 bar until the final pressure is one third its initial value.
- The gas undergoes an expansion against a constant external pressure of zero bar (free expansion) until the final pressure is equal to one third its initial value.

Soln.

Part(a)

$$\frac{T_f}{T_i} = \left(\frac{V_f}{V_i} \right)^{\gamma-1} = \left(\frac{P_i}{P_f} \right)^{\frac{\gamma-1}{\gamma}}$$

$$T_f = 298K \times (3.00)^{\frac{2}{5}} = 192K$$

$$\Delta U = w = 3 \times C_{v,m} (T_f - T_i) = -3.96kJ$$

$$\Delta H = \frac{5}{3} \Delta U = -6.6kJ$$

$$\Delta S = 0 \quad \text{because } q_{rev} = 0$$

Part(b)

$$W_{irr} = \Delta U$$

$$-P_{ext} \Delta V = 3 \times C_{v,m} \times (T_f - T_i)$$

$$-3R \times P_{ext} \left(\frac{T_f}{P_f} - \frac{T_i}{P_i} \right) = 3 \times C_{v,m} \times (T_f - T_i)$$

$$T_f = T_i \left(\frac{C_{v,m} + \frac{RP_{ext}}{P_i}}{C_{v,m} + \frac{RP_{ext}}{P_f}} \right) = 218.5K$$

$$\Rightarrow W_{irr} = \Delta U = 3 \times C_{v,m} \times (218.5K - 298K) = -2.974kJ$$

$$\Delta H = \frac{5}{3} \Delta U = -4.956kJ$$

$$q_{irr} = 0$$

$$\Delta S \neq 0!!!$$

ΔS is hard to measure, but we can choose two reversible process to reach the same final state.

$$\Delta S = -nR \ln \frac{P_f}{P_i} + nC_{p,m} \ln \frac{T_f}{T_i} = -3R \ln \frac{1}{3} + 3C_{p,m} \ln \frac{218.5}{298} = 8.08JK^{-1}$$

Part(c)

free expansion: $P_{\text{ext}} = 0$ and $\Delta T = 0$

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

$$\Delta H = 0$$

$$\Delta S = -nR \ln \frac{P_f}{P_i} = 27.4 \text{ JK}^{-1}$$

(15%) A gas sample behaves like the ideal gas containing 2 moles for which $C_{V,m} = 5/2 R$ undergoes the following reversible cyclical process from an initial state :
 $T = 275\text{K}$ and $P = 1.00 \text{ bar}$.

- (a) It is expanded reversibly and adiabatically until the volume triples.
- (b) It is reversibly heated at constant volume until T increases to 275K .
- (c) The pressure is increased in a reversible isothermal compression until pressure recover to 1.00bar

Calculate q , w , ΔU , ΔH , and ΔS and ΔS_{tot} for each process and whole cycle.

Soln.

Part(a)

$$\frac{T_f}{T_i} = \left(\frac{V_f}{V_i} \right)^{1-\gamma}$$

$$T_f = (3)^{-\frac{2}{5}} \times 275 \text{ K} = 177 \text{ K}$$

$$w = \Delta U = 2C_{V,m}(177 \text{ K} - 275 \text{ K}) = -4.07 \text{ kJ}$$

$$\Delta H = \frac{7}{5} \Delta U = -5.66 \text{ kJ}$$

$$q_{\text{rev}} = 0 \quad \Delta S = 0 \quad \Delta S_{\text{sur}} = 0 \quad \Delta S_i = 0$$

Part(b)

$$w = 0 \text{ (constant } V \text{)}$$

$$q = \Delta U = 2C_{v,m}(275\text{ K} - 177\text{ K}) = 4.073\text{ kJ}$$

$$\text{so } P_f = \frac{2 \times RT_f}{V_f} =$$

$$\Delta H = \frac{7}{5} \Delta U = 5703.4\text{ kJ}$$

$$\Delta S = 2R \ln \left(\frac{V_f}{V_i} \right) = 18.2\text{ JK}^{-1}$$

$$\Delta S_{sur} = \frac{-q}{T_{sur}} = \frac{4.073\text{ kJ}}{275\text{ K}} = -14.81\text{ JK}^{-1}$$

$$\Delta S_t = 3.39\text{ JK}^{-1}$$

$$\text{and so far you have } P_f = 0.33\text{ bar} = \frac{1}{3} P_0$$

$$\text{because } \frac{T_0 V_0}{P_0} = \frac{T_f V_f}{P_f} \text{ and } T_f = T_0 \quad V_f = 3V_0$$

Part(c)

reversible isothermal process

$$\Delta U = \Delta H = 0 \quad (\Delta T = 0)$$

$$w = -nRT \int_{V_i}^{V_f} \frac{1}{V} dV = -2 \times 8.314 \times 275 \times \ln \left(\frac{V_i}{3V_i} \right) = 5.0\text{ kJ}$$

$$q = -w = -5.0\text{ kJ}$$

$$\Delta S = \int \frac{dq_{rev}}{T} = \frac{1}{T} q = nR \ln \left(\frac{1}{3} \right) = -18.2\text{ JK}^{-1}$$

$$\Delta S_{sur} = \int \frac{-dq_{rev}}{T} = -\Delta S = 18.2\text{ JK}^{-1}$$

$$\Delta S_{tot} = 0$$

For whole cycle:

$$\Delta U_{cyc} = 0$$

$$\Delta S_{cyc} = 0$$

$$\Delta H_{cyc} = 0$$

$$\Delta S_{sur} = -14.81\text{ JK}^{-1} \quad 18.2\text{ JK}^{-1}$$

$$q_{cyc} = 927\text{ J}$$

$$\Delta S_t = \Delta S_{sur} + 0 = 3.4\text{ kJ}$$

$$w_{cyc} = -927\text{ J}$$

(20 %) The first law states that the energy of the universe is a constant ($\Delta U = q + w$) while the second law states that the entropy of the universe tends always towards a

maximum ($\Delta S_{\text{tot}} = \Delta S + \Delta S_{\text{surr}} \geq 0$). Answer the following questions *only* based on the conditions it is provided.

- (a) Assuming that the entropy change of the system is $\Delta S = \frac{q_{\text{rev}}}{T}$, determine the relationship of ΔS_{surr} in terms of q_{rev} and T . (3%)
- (b) If only PV -work is considered, prove that the inequality of work ($dw_{\text{rev}} < dw_{\text{irr}}$) is always valid (e.g., expansion or compression). (5%)
- (c) Prove $dq_{\text{rev}} > dq_{\text{irr}}$ based on $dw_{\text{rev}} < dw_{\text{irr}}$. (2%)
- (d) Based on $dq_{\text{rev}} > dq_{\text{irr}}$ to prove the Clausius inequality, $dS \geq \frac{dq}{T_{\text{surr}}}$, where the equality holds only for reversible processes. (3%)
- (e) Following (c) and (d) to prove that the entropy change of any irreversible process is always greater than zero in an isolated system. (3%)
- (f) Assuming that the system is no longer isolated, i.e., the surroundings are a reservoir of energy and the heat entering the system is equal to the heat leaving the surroundings. Show that the Clausius inequality can be deduced to a more general expression for the 2nd law, i.e., $dS_{\text{tot}} = dS + dS_{\text{surr}} \geq 0$. (4%)

Soln.

$$(a) \Delta S + \Delta S_{\text{surr}} \geq 0 \Rightarrow \Delta S_{\text{surr}} \geq -\Delta S = -\frac{q_{\text{rev}}}{T} \Rightarrow \Delta S_{\text{surr}} \geq -\frac{q_{\text{rev}}}{T}$$

$$(b) \left. \begin{aligned} \bar{dw}_{\text{rev}} &= -P dV \\ \bar{dw}_{\text{irr}} &= -P_{\text{ex}} dV \end{aligned} \right\} \bar{dw}_{\text{irr}} - \bar{dw}_{\text{rev}} = (P - P_{\text{ex}}) dV$$

① If expansion, $P > P_{\text{ex}}$ and $dV > 0$

$$\text{故 } (P - P_{\text{ex}}) dV > 0$$

② If compression, $P < P_{\text{ex}}$ and $dV < 0$

$$\text{故 } (P - P_{\text{ex}}) dV > 0$$

In any case, $(P - P_{\text{ex}}) dV > 0$

$$\text{故 } \bar{dw}_{\text{irr}} - \bar{dw}_{\text{rev}} > 0$$

$$\text{亦即 } \bar{dw}_{\text{rev}} < \bar{dw}_{\text{irr}}$$

$$(c) dU = dq_{\text{rev}} + dw_{\text{rev}} = dq_{\text{irr}} + dw_{\text{irr}}$$

$$\therefore dq_{\text{rev}} - dq_{\text{irr}} = dw_{\text{irr}} - dw_{\text{rev}} > 0$$

$$\therefore dq_{\text{rev}} > dq_{\text{irr}}$$

$$(d) \quad dq_{rev} = T dS = T_{surr} dS$$

$$\text{故 } T_{surr} dS > dq_{irr} \quad T_{surr} dS \geq dq$$

$$\text{and } T_{surr} dS = dq_{rev}$$

$$\Rightarrow dS \geq \frac{dq}{T_{surr}}$$

$$(e) \quad dS > \frac{dq_{irr}}{T_{surr}} = 0 \quad (\dot{dq}_{irr} = 0 \text{ for isolated system}) \Rightarrow dS \text{ (isolated system)} > 0$$

$$(f) \quad dS_{surr} = \frac{dq_{surr}}{T_{surr}} = \frac{-dq}{T_{surr}}$$

$$dS_{tot} = dS + dS_{surr} \geq \frac{dq}{T_{surr}} + \frac{-dq}{T_{surr}} = 0 \Rightarrow dS_{tot} \geq 0$$

(20%) You wish to construct a fuel cell based on oxidation of a hydrocarbon fuel. The two choices for a fuel are methane and octane. Calculate the maximum work available through the combustion of these two hydrocarbons, on a per mole and a per gram basis at 298.15 K and 1 bar pressure.

Useful thermodynamic data are the following:

	CH ₄ (g)	C ₈ H ₁₈ (l)	CO ₂ (g)	H ₂ O(l)	O ₂ (g)
ΔH_c^0 /kJ mol ⁻¹	-891	-5471	—	—	—
S_m^0 /J K ⁻¹ mol ⁻¹	186.3	361.1	213.8	70.0	205.2

Are there any other factors that should be taken into account in making a decision between these two fuels?

Soln.

$$dG = Vdp - SdT + dW'$$

$$\begin{aligned} dA &= -SdT + (dW_{pv} + dW') \\ &= -PdV - SdT + dW' \end{aligned}$$

Fuel cell: turning the chemical energy into electric energy.

You might choose one of them to represent the maximum electric energy you can get.

constant $T, V \Rightarrow dW' = dA$

constant $T, P \Rightarrow dW' = dG$ (this one will be better)

At constant T, P

$$dG = dH - TdS$$

$$\Delta G = \Delta H - T\Delta S$$

here $\Delta H = \Delta H_c^0$

$$\text{And } \Delta S = \sum S_{m, \text{product}}^0 - \sum S_{m, \text{reactant}}^0$$

For CH_4 :

$$\Delta G = -891 \text{ kJ} - \frac{298 \times (2 \times 70 + 213.8 - 2 \times 205.2 - 186.3)}{1000 \text{ J / kJ}} = -818 \text{ kJ / mol} \cong -36 \text{ kJ / L}$$

For C_8H_{18} :

$$\Delta G = -5471 \text{ kJ} - \frac{298 \times (9 \times 70 + 8 \times 213.8 - 12.5 \times 205.2 - 361.1)}{1000 \text{ J / kJ}} = -5294 \text{ kJ / mol} \cong -815 \text{ kJ / L}$$

And when we talk about the storage

We want to know $\frac{\text{kJ}}{\text{L}}$

Because the liquid is much easier to storage and more stable,

We will choose the Octane.