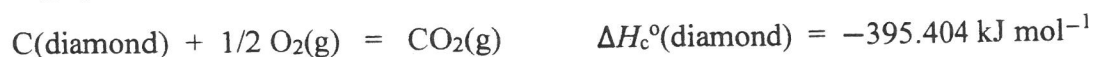
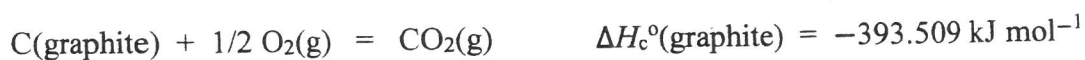


1. a) 100.0 L of helium (assumed to be an ideal gas) initially at 1.00 bar and 300 K is compressed isothermally with $p_{\text{ext}} = p$ to a final pressure of 10.0 bar. Calculate q , w , ΔU and ΔS .
- [4] b) The Second Law gives $(\Delta S = 0)_{\text{isolated system}}$ for a reversible process in an isolated system. Use this criterion to prove the gas expansion described in part a is reversible. (*Hint*: The gas is not an isolated system, but the gas + surroundings taken together form an isolated system.)

2. a) 100.0 L of helium (assumed to be an ideal gas) initially at 1.00 bar and 300 K is compressed isothermally with $p_{\text{ext}} = 10.0$ bar to a final pressure of 10.0 bar. Calculate q , w , ΔU and ΔS .
- [4] b) The Second Law gives $(\Delta S > 0)_{\text{isolated system}}$ for an irreversible process in an isolated system. Use this criterion to prove the gas expansion described in part a is irreversible.

3. Precise calorimetric measurements give



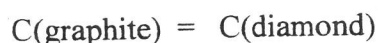
- [2] for the enthalpies of combustion of graphite and diamond at 25 °C and 1 bar. Use the combustion data to show the standard enthalpy of formation of diamond at 25 °C is



4. Precise heat capacities have been measured for graphite and diamond. Explain briefly how the Third Law and the heat capacity data are used to calculate the absolute entropies of graphite and diamond at 25 °C and 1 bar:

[2] $S_{\text{m}}^{\circ}(\text{graphite}) = 5.740 \text{ J K}^{-1} \text{ mol}^{-1}$ $S_{\text{m}}^{\circ}(\text{diamond}) = 2.377 \text{ J K}^{-1} \text{ mol}^{-1}$

5. For the conversion of graphite to diamond at 25 °C and 1 bar



- [4] a) calculate q and ΔS (use data given in Questions 2 and 3)
 b) use $(\Delta S \geq 0)_{\text{isolated system}}$ to decide if conversion is spontaneous or nonspontaneous.

6. In a modern combined cycle electricity generating station, natural gas is used to run a high-temperature gas turbine with $T_{\text{H}} = 1600 \text{ K}$, $T_{\text{C}} = 800 \text{ K}$. Hot exhaust at 800 K from the gas turbine is used to run a steam turbine with $T_{\text{H}} = 800 \text{ K}$, $T_{\text{C}} = 300 \text{ K}$. Calculate:

- [4] a) the maximum efficiency of the gas turbine
 b) the maximum efficiency of the steam turbine
 c) the maximum combined efficiency of the gas and steam turbines operating in tandem
 d) the maximum work done on the surroundings for every 1.00 MJ heat absorbed at 1600 K.
 (*Hint*: q_{H} for the steam turbine equals $-q_{\text{C}}$ for the gas turbine)

(Q1) 100.0 L of helium (assumed to be an ideal gas) at 1.00 bar, 300 K is isothermally compressed to 10.0 bar with $P_{\text{ext}} = P$.

a)

$$w = - \int P_{\text{ext}} dV = - \int p dV = - \int_{V_i}^{V_f} \frac{nRT}{V} dV = - nRT \int_{V_i}^{V_f} \frac{1}{V} dV$$

(isothermal)

$$V_i = 100.0 \text{ L} \quad P_i V_i = P_f V_f = nRT$$

$$V_f = \frac{P_i}{P_f} V_i = \frac{1.00 \text{ bar}}{10.0 \text{ bar}} 100.0 \text{ L} = 10.0 \text{ L}$$

$$w = - nRT \ln \left(\frac{V_f}{V_i} \right) = - P_i V_i \ln \left(\frac{V_f}{V_i} \right)$$

$$= - (1.00 \text{ bar})(100.0 \text{ L}) \ln \left(\frac{10.0 \text{ L}}{100.0 \text{ L}} \right)$$

$$= 230.2 \text{ L bar} = (230.2 \text{ L bar}) \left(\frac{100 \text{ J}}{\text{L bar}} \right)$$

$$w = 23020 \text{ J}$$

$$\Delta U = 0 \quad (\text{isothermal ideal gas})$$

($dU = C_V dT = C_V(0) = 0$)

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

$$q = -w$$

$$q = -23,020 \text{ J}$$

$P = P_{\text{ext}} \Rightarrow$ this means the compression is reversible

$$\Delta S = \int \frac{1}{T} dq_{\text{rev}} = \frac{1}{T} \int dq_{\text{rev}} = \frac{q_{\text{rev}}}{T} \quad (q = q_{\text{rev}})$$

$$\Delta S = \frac{-23020 \text{ J}}{300 \text{ K}} = -76.73 \frac{\text{J}}{\text{K}}$$

(Q1 a) conti.)

Not sure if the process is reversible?

No problem! The entropy S is a state function, so any path can be used to calculate ΔS .

For convenience, take a reversible path: $dq_{rev} = TdS$
 $dw_{rev} = -pdv$

$$dU = C_v dT = dq_{rev} + dw_{rev}$$

$$\frac{C_v dT}{T} = \frac{dq_{rev}}{T} + \frac{dw_{rev}}{T} \quad \left(\begin{array}{l} \text{isothermal} \\ dT=0 \end{array} \right)$$

$$0 = dS - \frac{pdv}{T}$$

$$\Delta S = \int dS = \int \frac{p}{T} dv = \int \frac{nRT}{V T} dv$$

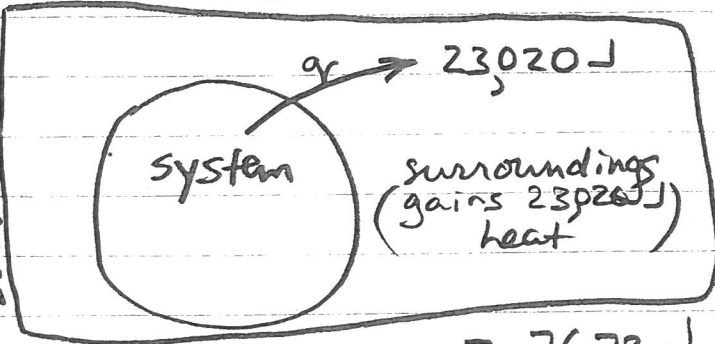
$$\Delta S = nR \int \frac{1}{V} dv = \frac{nRT \int \frac{dv}{V}}$$

$$= \frac{nRT \ln\left(\frac{V_f}{V_i}\right)}{T} = \frac{-23,020 \text{ J}}{300 \text{ K}} = -76.73 \frac{\text{J}}{\text{K}}$$

0

$(\Delta S_{sys} + \Delta S_{sur})_{isolated} = 0$
 \therefore Reversible

b) The system is not isolated, but the system + surround is isolated

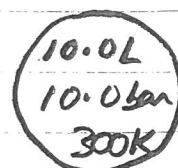
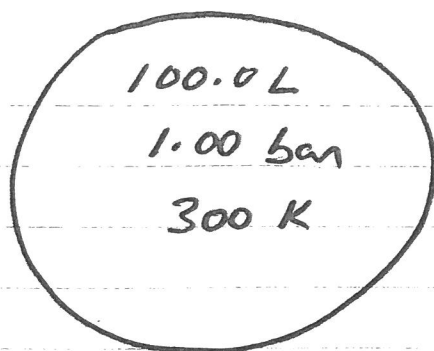


$(\Delta S_{system} + \Delta S_{sur.})_{isolated}$

$$= -76.73 \frac{\text{J}}{\text{K}} + \frac{q_{sum}}{T_{sum}}$$

$$= -76.73 \frac{\text{J}}{\text{K}} + \frac{23,020 \text{ J}}{300 \text{ K}} = -76.73 + 76.73 \frac{\text{J}}{\text{K}} = 0$$

Q2



100.0 L of helium at 1.00 bar, 300 K is compressed isothermally to 10.0 bar with $P_{ext} = 10.0 \text{ bar}$

a)

Note: same initial and final states as in Q1, so

$\Delta U = 0$	} path-independent (U, S are state functions)
$\Delta S = -76.73 \text{ J K}^{-1}$	

$$W = - \int P_{ext} dV = - P_{ext} \int dV = - P_{ext} (V_f - V_i)$$

(1 L bar = 100 J)

$$W = -(10.0 \text{ bar})(10.0 - 100.0) \text{ L} = 900 \text{ L bar}$$

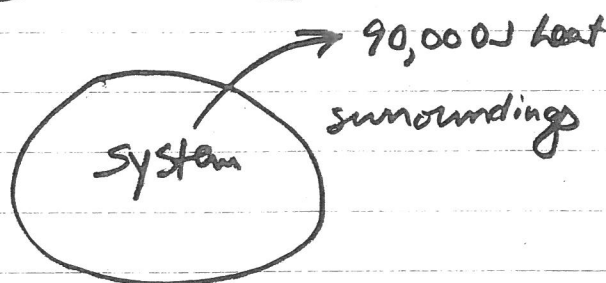
$$W = 90,000 \text{ J}$$

$$q = -90,000 \text{ J}$$

$$\Delta U = 0 = q + W$$

$$q = -W$$

b)



important:

$$\frac{q}{T} = \frac{-90,000 \text{ J}}{300 \text{ K}}$$

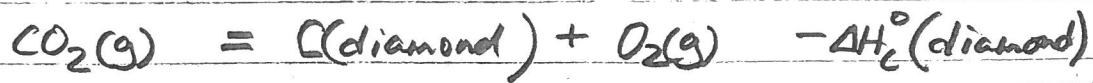
$$= -300 \frac{\text{J}}{\text{K}}$$

$$\neq \Delta S_{sys} \quad q \text{ not rev.}$$

$$(\Delta S_{sys} + \Delta S_{sum})_{isolated} = -76.73 \frac{\text{J}}{\text{K}} + \frac{q_{sum}}{T_{sum}}$$

$$= -76.73 \frac{\text{J}}{\text{K}} + \frac{90,000 \text{ J}}{300 \text{ K}} = (-76.73 + 300.0) \frac{\text{J}}{\text{K}} = 223 \frac{\text{J}}{\text{K}}$$

> 0
∴ spont.



$$\Delta H_f^\circ(\text{diamond}) = \Delta H_c^\circ(\text{graphite}) - \Delta H_c^\circ(\text{diamond})$$

$$= -393.509 - (-395.404) \text{ kJ mol}^{-1}$$

$$= \boxed{1.895 \text{ kJ mol}^{-1}}$$

Q4 According to the Third Law, the entropies "absolute" of graphite and diamond at $T = 0 \text{ K}$ (zero) are zero (perfect crystals at 0 K).

$$S_m^\circ(\text{graphite}, T) = S_m^\circ(\text{graphite}, 0 \text{ K}) + \int_{T=0}^T dS$$

$$= \int_{T=0}^T \frac{dq_{\text{rev},m}}{T}$$

$$S_m^\circ(\text{graphite}, T) = \int_{T=0}^T \frac{C_{p,m}^\circ(\text{graphite})}{T} dT$$

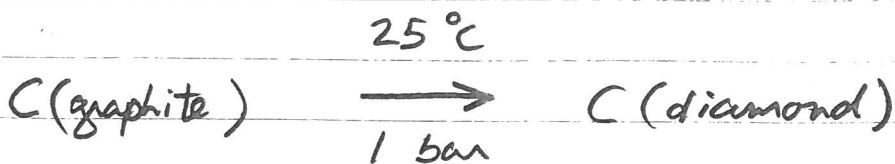
at $p^\circ = 1 \text{ bar}$
 $\frac{dq}{dT} = C_p^\circ$
 $dq = C_p^\circ dT$

Similarly:

$$S_m^\circ(\text{diamond}, T) = \int_{T=0}^T \frac{C_{p,m}^\circ(\text{diamond})}{T} dT$$

absolute entropies per mole at 1.00 bar standard pressure and temperature T

Q5



a)

$$\begin{aligned} \Delta H^\circ &= q_{\text{(const. p)}} = \Delta H_{\text{fm}}^\circ(\text{diamond}) - \Delta H_{\text{fm}}^\circ(\text{graphite}) \\ &= 1.895 \text{ kJ mol}^{-1} - 0 \end{aligned}$$

← (elemental carbon in its stable state)

$$\begin{aligned} \Delta S^\circ &= S_m^\circ(\text{diamond}) - S_m^\circ(\text{graphite}) \\ &= (2.377 - 5.740) \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

$$\Delta S^\circ = -3.363 \text{ J K}^{-1} \text{ mol}^{-1}$$

b) Is the conversion of graphite to diamond spontaneous at 25 °C, 1 bar?

Note: Can't use $\Delta S^\circ < 0$ alone to answer this question because the system (graphite and diamond) is not isolated

system

1.895 kJ heat surroundings

$$(\Delta S_{\text{system}} + \Delta S_{\text{surv.}})_{\text{isolated}}$$

$$= -3.363 \frac{\text{J}}{\text{K mol}} + \frac{-1895 \text{ J}}{298.15 \text{ K}}$$

$$= (-3.363 - 6.356) \text{ J K}^{-1} \text{ mol}^{-1}$$

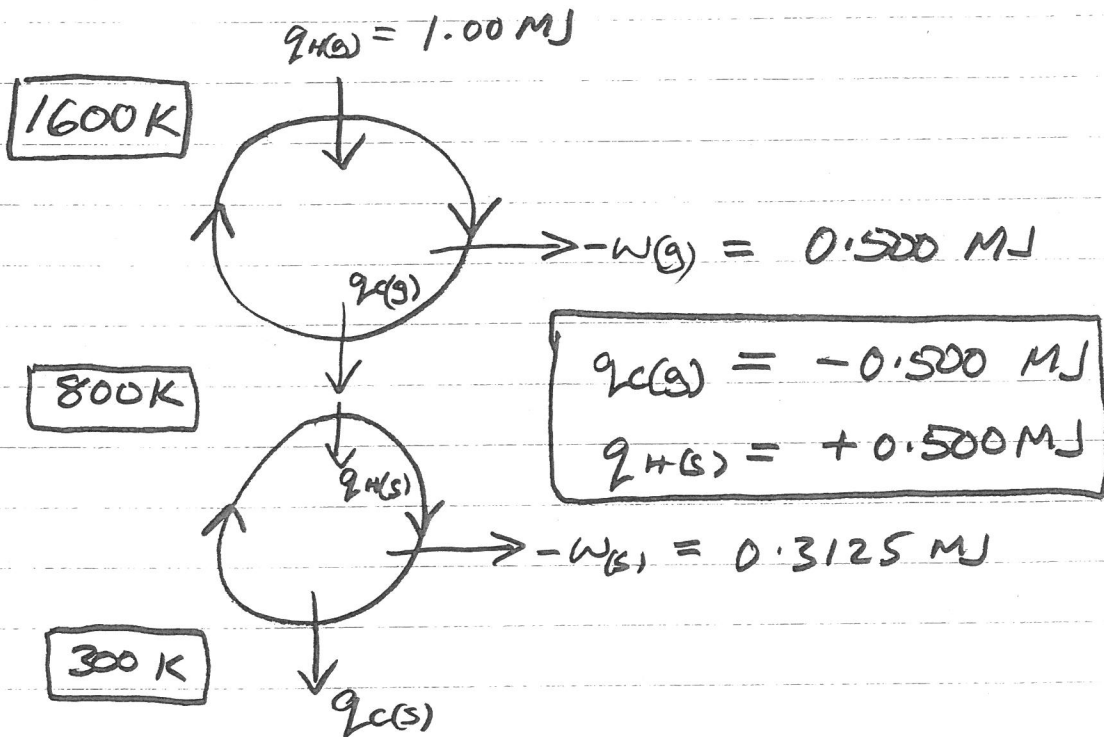
$$= -9.719 \text{ J K}^{-1} \text{ mol}^{-1} \text{ impossible!}$$

⇒ the conversion will not happen

Find $\Delta S < 0$ for isolated system + surr.
⇒ not spont.

(Q5 d) cont.)

more detailed answer (not required!):



gas turbine $\epsilon_{\max(g)} = 1 - \frac{800 \text{ K}}{1600 \text{ K}} = 0.500 = \frac{-W(g)}{q_{H(g)}}$

$$-W(g) = 0.500 q_{H(g)} = 0.500 (1.00 \text{ MJ}) = 0.500 \text{ MJ}$$

$$q_{H(g)} + W(g) + q_{C(g)} = 0$$

$$q_{C(g)} = -q_{H(g)} - W(g) = (-1.00 + 0.500) \text{ MJ} = -0.500 \text{ MJ}$$

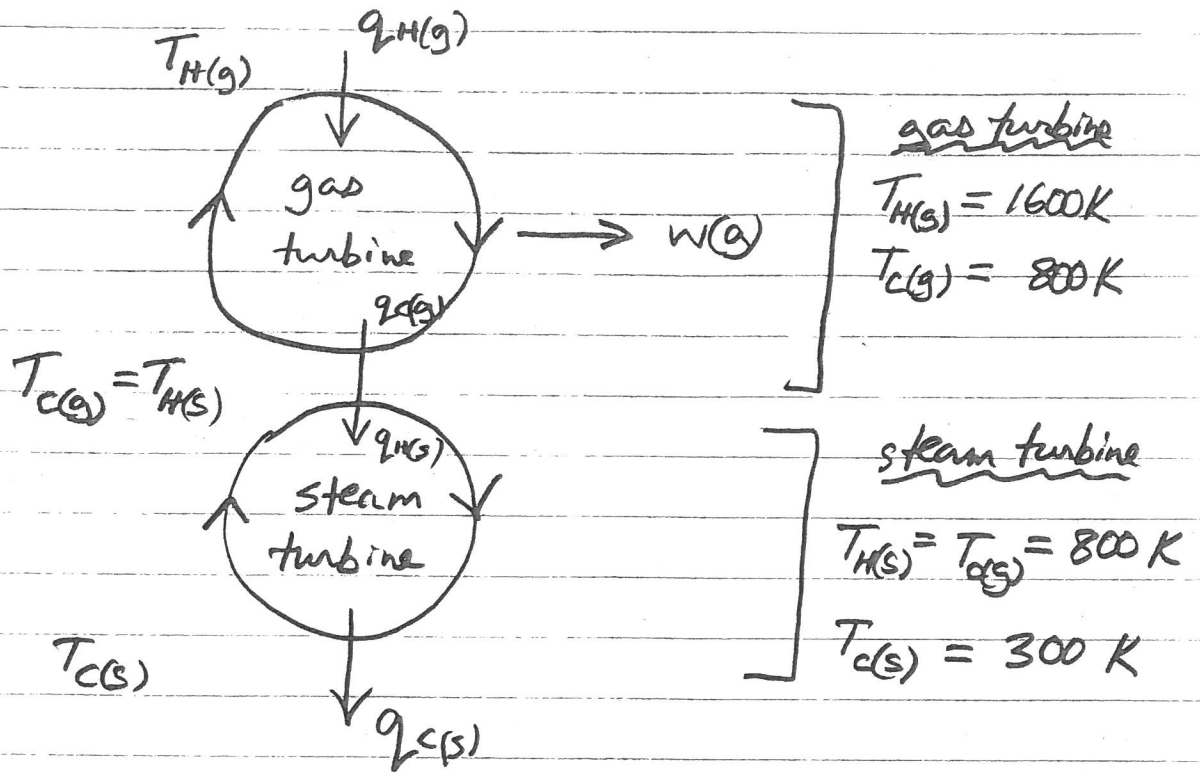
steam turbine $\epsilon_{\max(s)} = 1 - \frac{300 \text{ K}}{800 \text{ K}} = 0.625$

$$0.625 = \frac{-W(s)}{q_{H(s)}}$$

$$-W(s) = 0.625 q_{H(s)} = 0.625 (0.500 \text{ MJ}) = 0.3125 \text{ MJ}$$

max work overall $= -W(g) - W(s) = (0.500 + 0.3125) \text{ MJ} = 0.8125 \text{ MJ}$

Q6



a) gas turbine $\epsilon_{\max(g)} = 1 - \frac{T_{C(g)}}{T_{H(g)}} = 1 - \frac{800K}{1600K} = \boxed{0.500}$

for rev. heat engines

b) steam turbine $\epsilon_{\max(s)} = 1 - \frac{T_{C(s)}}{T_{H(s)}} = 1 - \frac{300K}{800K} = \boxed{0.625}$

c) heat absorbed at 1600 K, heat rejected at 300 K

$$\epsilon_{\max, \text{overall}} = 1 - \frac{300K}{1600K} = \boxed{0.8125} = \frac{-W_{\text{overall}}}{q_{H(g)}}$$

d) $q_{H(g)} = 1.00 \text{ MJ}$

max. work done on the surroundings $-W_{\text{overall}} = 0.8125(1.00 \text{ MJ}) = \boxed{0.8125 \text{ MJ}}$