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*Final exam from*  
*2004*

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1) Liquid water enters an adiabatic piping system at 15 °C at a rate of 5 kg/s. Assume water to be an incompressible substance with a specific heat of 4.18 kJ/kg.K. If the water temperature rises by 0.5 °C during the flow due to friction, the rate of entropy heat generation in the pipe is

- (a) 36 W/K            (b) 29 W/K            (c) 685 W/K            (d) 920 W/K  
(e) 8370 W/K

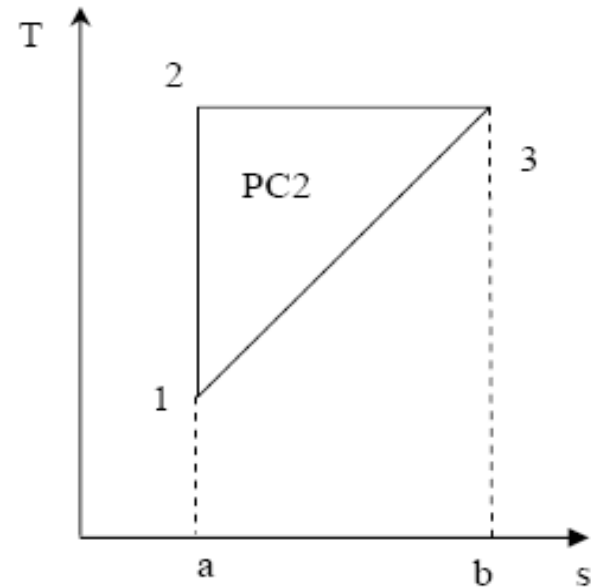
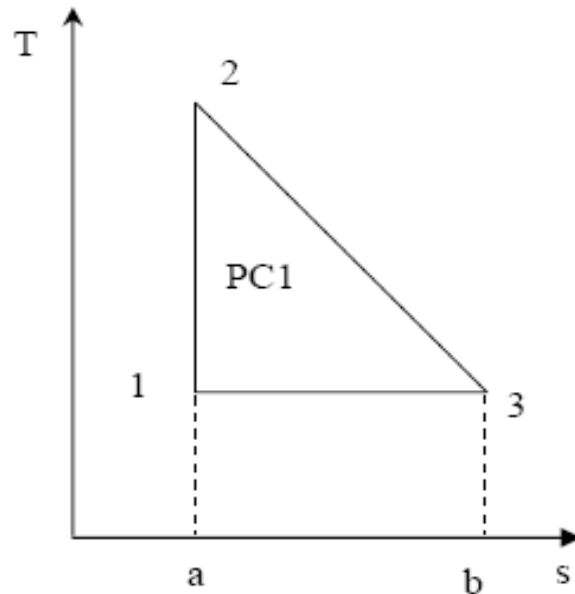
Solution:

(a) 36 W/K

The rate of entropy generation is given by

$$\dot{S}_{gen} = \dot{m}C \ln \frac{T_2}{T_1} = 5 * 4.18 * \ln \frac{288.5}{288} \approx 36 \text{ W / K}$$

2) Which cycle has the greater thermal efficiency? (a) PC1 (b) PC2



You may assume that both have same scales and operate between same temperatures, and that both cycles are internally reversible.

$$\begin{aligned} \text{The thermal efficiency} &= \text{Work}/(\text{Heat from hot reservoir}) \\ &= \text{area}(1-2-3-1)/\text{area}(a-2-3-b-a) \end{aligned}$$

In both power cycles, from assumption 1, the area (1-2-3-1) is the same. Now, it can be seen that

$$(\text{area}(a-2-3-b-a))_{\text{PC1}} < (\text{area}(a-2-3-b-a))_{\text{PC2}}$$

Therefore,  $\eta_{\text{PC1}} > \eta_{\text{PC2}}$

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3) A heat engine receives heat from a source at  $1200\text{ K}$  at a rate of  $500\text{ kJ/s}$  and rejects the waste heat to a sink at  $300\text{ K}$ . If the power output of the engine is  $200\text{ kW}$ , the second law efficiency (actual work divided by the maximum possible work) of this heat engine is

- (a) 35 %                      (b) 40 %                      (c) 53 %                      (d) 75 %                      (e) 100 %

The maximum possible thermal efficiency of this heat engine:

$$\eta_{\max} = 1 - T_C/T_H = 0.75.$$

The maximum possible power output of the engine,

$$W_{\max} = \eta_{\max} * Q_{in} = 375\text{ kW}$$

The second law efficiency is given by  $\eta_{II} = \frac{W_{\text{actual}}}{W_{\max}} \simeq 53\%$

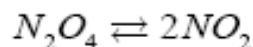
4) Consider the dissociation of  $N_2O_4$  to  $NO_2$  at  $p = 1$  atm with 1 kmol of  $N_2O_4$  present initially,  $N_2O_4 \rightleftharpoons 2NO_2$ . If  $x$  kmol of  $N_2O_4$  dissociates into  $NO_2$  at equilibrium, then the correct expression for the equilibrium constant  $K$  is

(a)  $K = \frac{x^2}{1-x}$       (b)  $K = \frac{4x^2}{1-x}$       (c)  $K = \frac{4x^2}{1-x^2}$       (d)

$K = \frac{8x^2}{1-x^2}$

(e)  $K = \frac{x^2}{1-x^2}$

$x$  kmol of  $N_2O_4$  dissociates to give  $2x$  kmol  $NO_2$  at equilibrium.

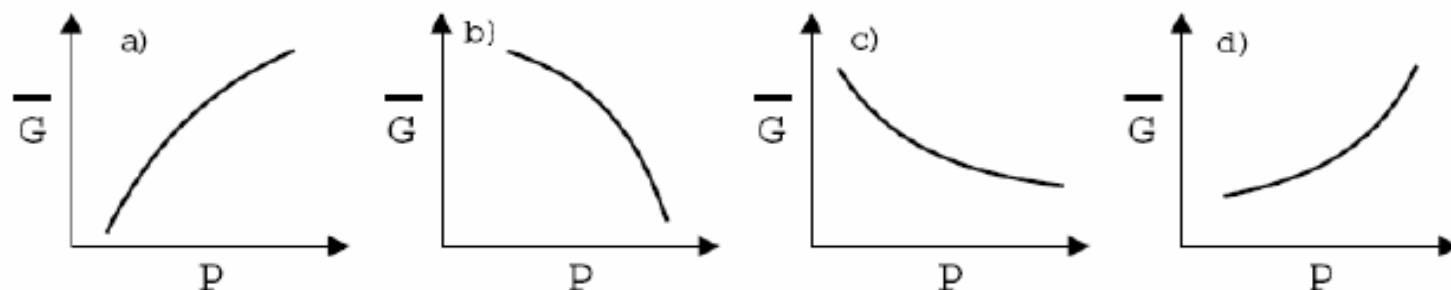


1-x      2x      (equilibrium)

Total number of moles = 1-x + 2x = 1 + x

$$K = \frac{(2x/(1+x))^2}{((1-x)/(1+x))} \left( \frac{p}{p_{ref}} \right)^{2-1} = \frac{4x^2}{1-x^2}$$

5) Select the figure below that illustrates the correct dependence of the molar Gibbs free energy  $\bar{G}$ , on pressure, P, at constant temperature for a single component solid. Explain your choice.



Starting from the differential expression for  $\bar{G}$ , we can write expressions for slope and curvature.

$$d\bar{G} = -\bar{S}dT + \bar{V}dp \Rightarrow \left(\frac{\partial \bar{G}}{\partial P}\right)_T = \bar{V} \quad \text{and} \quad \left(\frac{\partial^2 \bar{G}}{\partial P^2}\right)_T = \left(\frac{\partial \bar{V}}{\partial P}\right)_T = -\beta_T \bar{V}$$

The slope is positive. This eliminates (b) and (c).

$\beta_T > 0$  and therefore the curvature is negative. This eliminates choice (d).

Therefore, curve (a) is the right answer since it gives the correct slope and curvature.

## Problem 2 (20 points)

Evaluate the equilibrium constant at 2000 K for the reaction  $CH_4 + H_2O \rightleftharpoons 3H_2 + CO$ . At 2000 K the following data is given:

(i) for the reaction  $C + \frac{1}{2}O_2 \rightleftharpoons CO$ ,  $\log_{10}K = 7.469$

(ii) for the reaction  $C + 2H_2 \rightleftharpoons CH_4$ ,  $\log_{10}K = -3.408$

(iii) for the reaction  $H_2O \rightleftharpoons H_2 + \frac{1}{2}O_2$ ,  $\log_{10}K = -3.54$

For reaction (i), we have,  $\Delta G_{(i)}^0 = g_{CO}^0 - g_C^0 - \frac{1}{2}g_{O_2}^0$  .....(1)

For reaction (ii), we have  $\Delta G_{(ii)}^0 = g_{CH_4}^0 - g_C^0 - 2g_{H_2}^0$  .....(2)

For reaction (iii), we have  $\Delta G_{(iii)}^0 = g_{H_2}^0 + \frac{1}{2}g_{O_2}^0 - g_{H_2O}^0$  .....(3)

Subtracting (2) from (1) and adding (3) to it, we get

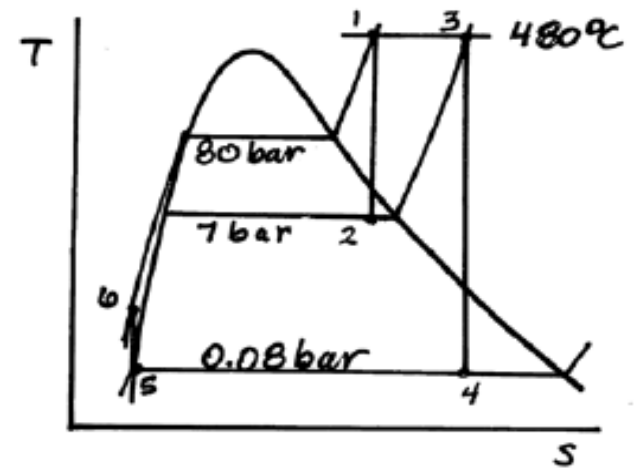
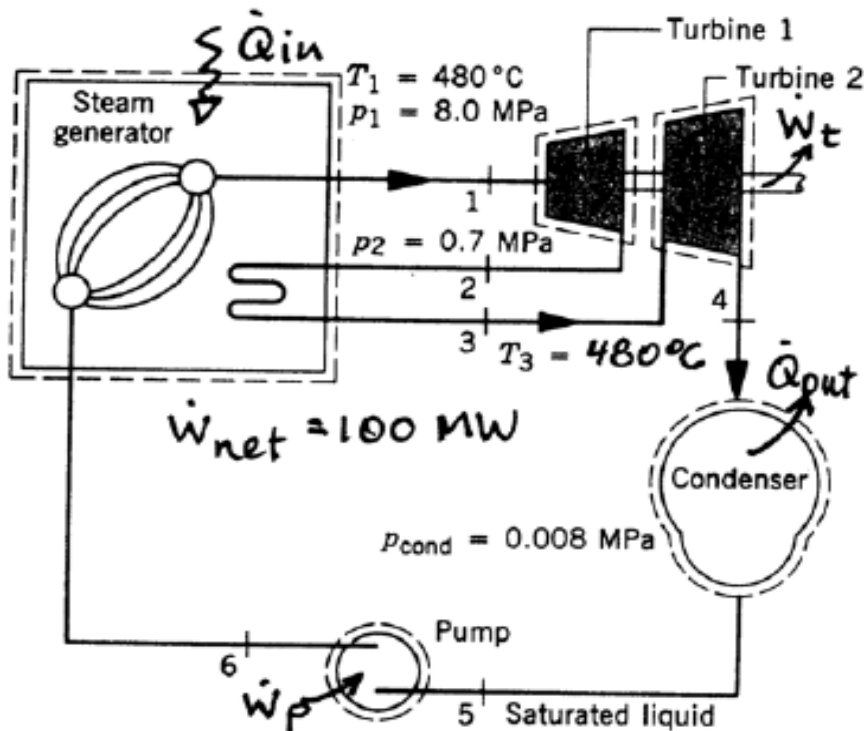
$$\Delta G_{(iv)}^0 = \Delta G_{(i)}^0 - \Delta G_{(ii)}^0 + \Delta G_{(iii)}^0 = 3g_{H_2}^0 + g_{CO}^0 - g_{CH_4}^0 - g_{H_2O}^0$$

Accordingly,  $\frac{\Delta G_{(iv)}^0}{RT} = \frac{\Delta G_{(i)}^0}{RT} - \frac{\Delta G_{(ii)}^0}{RT} + \frac{\Delta G_{(iii)}^0}{RT} \Rightarrow \ln K_4 = \ln K_1 - \ln K_2 + \ln K_3$

or,  $\log_{10} K_4 = \log_{10} K_1 - \log_{10} K_2 + \log_{10} K_3 = 7.469 - (-3.408) + (-3.54) = 7.337$   
 $\Rightarrow K_4 = 2.173 \times 10^7$

Steam at 8.0 MPa, 480 °C enters the first stage of a supercritical reheat cycle including two turbine stages. The steam, exiting the first stage at 0.7 MPa, is reheated at constant pressure to 480 °C before entering the second stage. The condenser pressure is 0.008 MPa and the net power output of the cycle is 100 MW. Assuming the isentropic efficiencies of both the turbine stages and the pump to be 100 %, determine

- the mass flow rate of the working fluid.
- the rate of heat transfer to the working fluid passing through the steam generator, in MW.
- the thermal efficiency.
- the rate of heat transfer in the condenser, in MW.



State 1:  $h_1 = 3348.4$  kJ/kg,  $s_1 = 6.6586$  kJ/kg.K

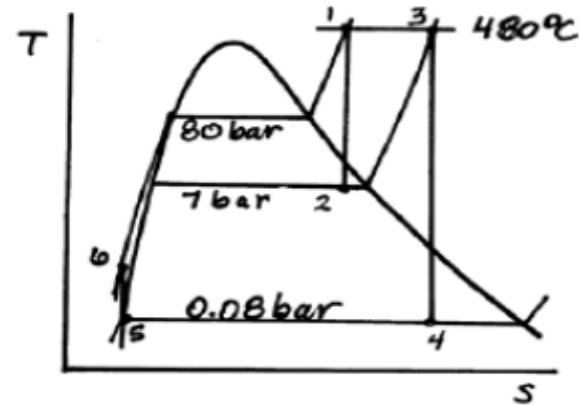
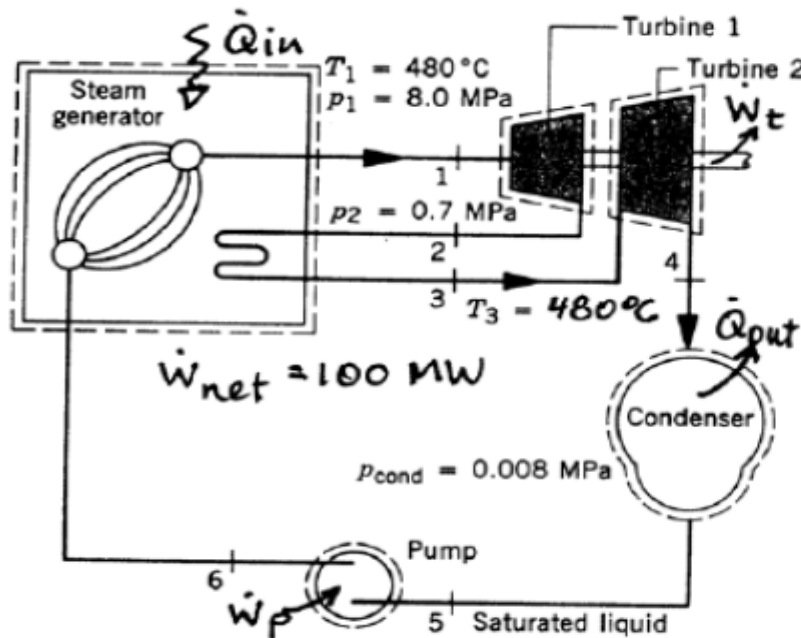
State 3:  $h_3 = 3438.9$  kJ/kg,  $s_3 = 7.8723$  kJ/kg.K

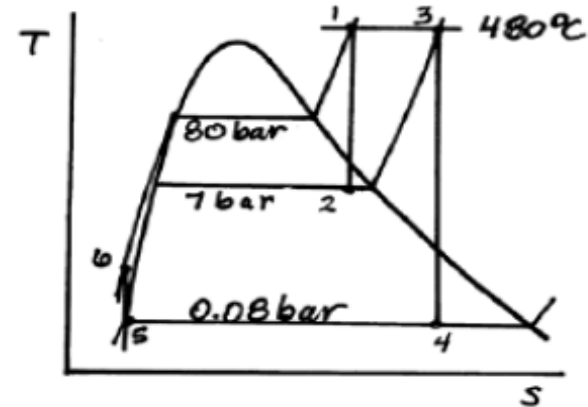
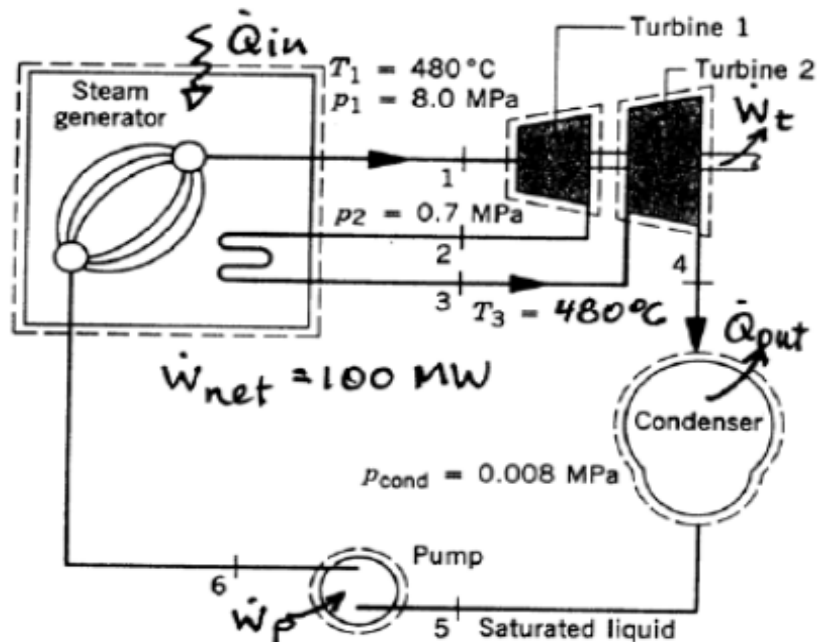
Properties of saturated water (liquid-vapor):

Pressure (bar)	Specific Volume (m <sup>3</sup> /kg)		Specific enthalpy (kJ/kg)		Specific entropy (kJ/kg.K)	
	Sat. liquid $v_f \times 10^3$	Sat. vapor $v_g$	Sat. liquid $h_f$	Sat. vapor $h_g$	Sat. liquid $s_f$	Sat. vap. $s_g$
0.08	1.0084	18.103	173.88	2577.0	0.5926	8.2287
7	1.1080	0.2729	697.22	2763.5	1.9922	6.7080

State 1:  $p_1 = 80 \text{ bar}$ ,  $T_1 = 480^\circ\text{C}$ , so from Table A-4,  $h_1 = 3348.4 \text{ kJ/kg}$  (given) and  $s_1 = 6.6586 \text{ kJ/kg}$  (given)

State 2:  $p_2 = 7 \text{ bar}$ . Since the turbine efficiency is 100%, the expansion process in the turbine is isentropic. Therefore,  $s_2 = s_{2s} = s_1 = 6.6586 \text{ kJ/kg}$ . From interpolation in Table A-3,  $x_2 = 0.9895$  and  $h_2 = 2741.8 \text{ kJ/kg}$ .

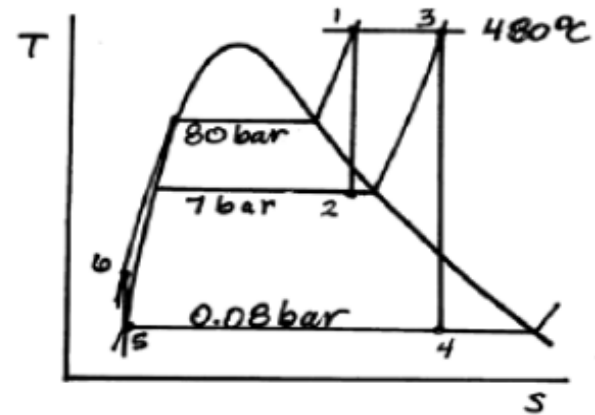
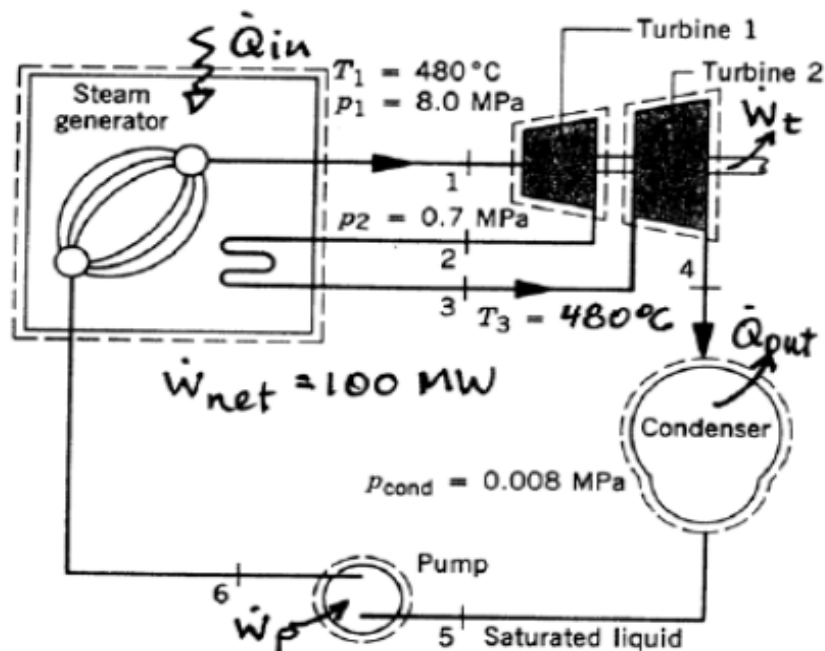




State 3:  $p_3 = 7 \text{ bar}$ ,  $T_3 = 480 \text{ }^\circ\text{C}$ , so from Table A-4,  $h_3 = 3438.9 \text{ kJ/kg}$  (given) and  $s_3 = 7.8723 \text{ kJ/kg}\cdot\text{K}$  (given)

State 4:  $p_4 = 0.08 \text{ bar}$ . Going through the same analysis as for the first turbine stage:

$s_4 = s_{4s} = s_3 = 7.8723 \text{ kJ/kg}\cdot\text{K}$ . From interpolation in Table A-3,  $x_4 = 0.9533$  and  $h_4 = 2464.8 \text{ kJ/kg}$ .



State 5:  $p_5 = p_4 = 0.08 \text{ bar}$ , and the water is a saturated liquid at the exit of the condenser, so  $h_5 = 173.88 \text{ kJ/kg}$  and  $s_5 = 0.5926 \text{ kJ/kg.K}$

State 6:  $p_6 = p_1 = 80 \text{ bar}$ .

$$h_6 = h_5 + v_5(p_6 - p_5) = 173.88 \text{ kJ/kg} + (1.0084 \times 10^{-3}) \frac{\text{m}^3}{\text{kg}} (80 - 0.08) \left( \frac{10^5 \text{ Nm}^{-2}}{1 \text{ bar}} \right) \left( \frac{1 \text{ kJ}}{10^3 \text{ Nm}} \right)$$

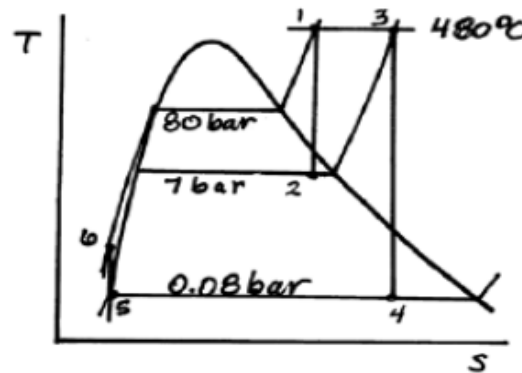
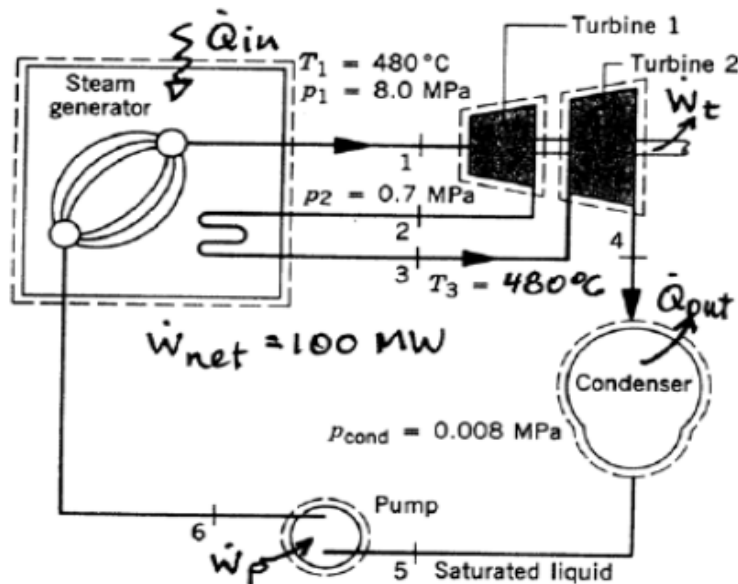
$$= 173.88 + 8.06 \text{ kJ/kg} = 181.94 \text{ kJ/kg}$$

(a) Next, given the net power output, the mass flow rate of the working fluid can be found out as follows:

$$\dot{W}_{net} = \dot{W}_{t1} + \dot{W}_{t2} - \dot{W}_p = \dot{m}[(h_1 - h_2) + (h_3 - h_4) - (h_6 - h_5)]$$

$$\dot{m} = \frac{\dot{W}_{net}}{(h_1 - h_2) + (h_3 - h_4) - (h_6 - h_5)} = \frac{(100MW) \left( \frac{1000 \text{ kJs}^{-1}}{1MW} \right)}{[(3348.4 - 2741.8) + (3438.9 - 2464.8) - 8.06] \text{ kJ/kg}}$$

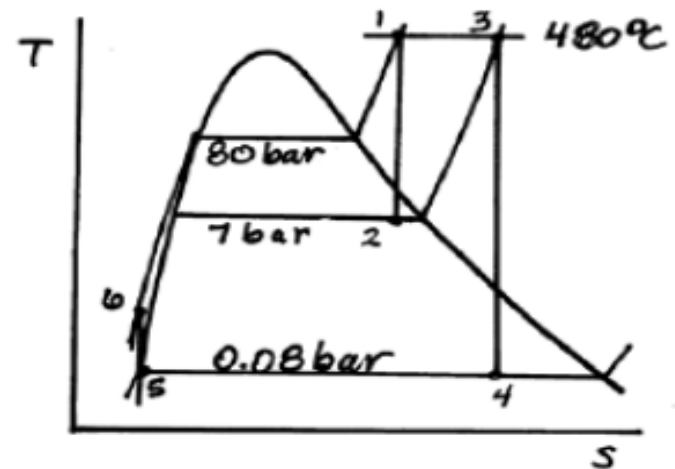
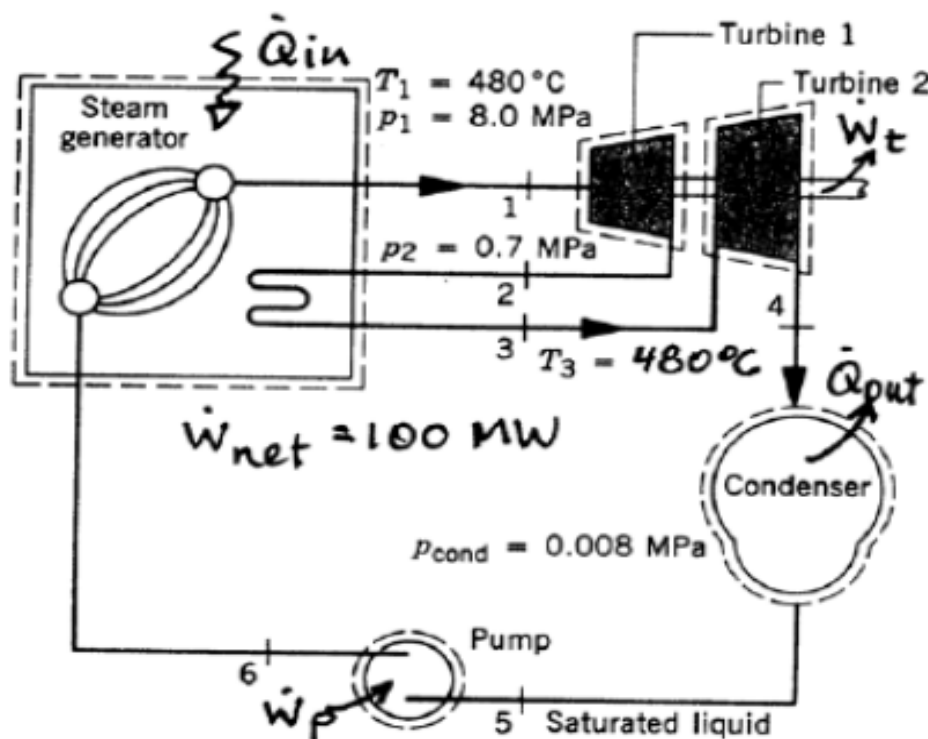
$$= \underline{63.587 \frac{\text{kg}}{\text{s}}}$$



(b) Using the energy rate balance with assumptions (1) and (5), the rate of heat transfer to the working fluid in the steam generator is

$$\dot{Q}_{in} = \dot{m}(h_1 - h_6 + h_3 - h_2) = 63.587 \frac{\text{kg}}{\text{s}} (3348.4 - 181.94 + 3438.9 - 2741.8) \frac{\text{kJ}}{\text{kg}}$$

$$= \underline{245.67 \text{ MW}}$$



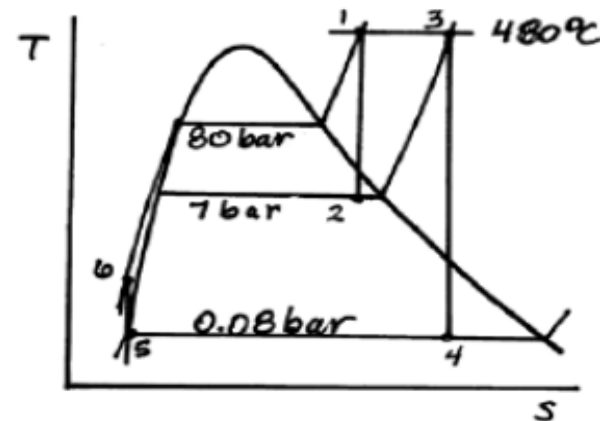
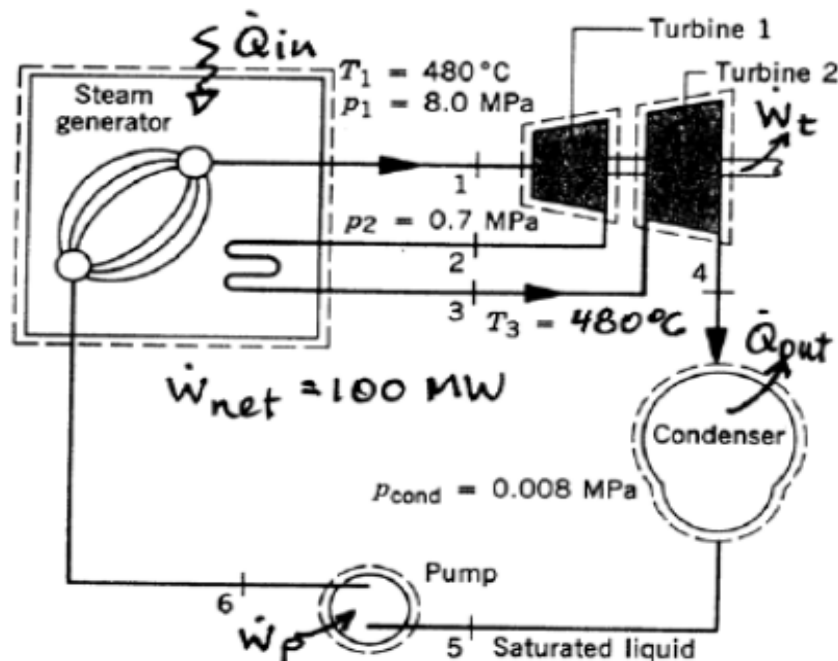
(c) Using the same assumptions, the rate of heat transfer in the condenser

$$\dot{Q}_{out} = m(h_4 - h_5) = (63.587) \frac{kg}{s} (2464.8 - 173.88) \frac{kJ}{kg} \left( \frac{1 MW}{1000 kJ/s} \right) = \underline{145.67 MW}$$

or,  $\dot{Q}_{out} = \dot{Q}_{in} - \dot{W}_{cycle} = \underline{145.67 MW}$

(d) The cycle thermal efficiency is

$$\eta = \frac{\dot{W}_{net}}{\dot{Q}_{in}} = \frac{100 MW}{245.67 MW} = 0.407 = \underline{40.7\%}$$



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**Problem 4 (15 points)**

Show that the relation that describes the dependence of entropy  $S$  on the Gibb's Free energy  $G$  and enthalpy  $H$  is the following:

$$dS = \frac{-C_p}{TS(1-T\alpha) + TC_p} dG + \frac{C_p - T\alpha S}{TS(1-T\alpha) + TC_p} dH$$

**Hint:** Use the relationship  $dS = \left(\frac{\partial S}{\partial G}\right)_H dG + \left(\frac{\partial S}{\partial H}\right)_G dH$  and evaluate the terms inside the brackets using the method of Jacobians. Some important relationships:

$$\begin{aligned}dG &= -SdT + VdP & dS &= \frac{C_p}{T}dT - V\alpha dP \\dH &= C_p dT + V(1 - T\alpha)dP\end{aligned}$$

$$dS = \left( \frac{\partial S}{\partial G} \right)_H dG + \left( \frac{\partial S}{\partial H} \right)_G dH \quad (1)$$

$$\left( \frac{\partial S}{\partial G} \right)_H = \frac{\begin{vmatrix} S_T & H_T \\ S_P & H_P \end{vmatrix}}{\begin{vmatrix} G_T & H_T \\ G_P & H_P \end{vmatrix}} = \frac{S_T H_P - S_P H_T}{G_T H_P - G_P H_T}$$

$$\begin{aligned} \left( \frac{\partial S}{\partial G} \right)_H &= \frac{\left( \frac{C_P}{T} \right) (V(1-T\alpha)) - (-V\alpha)(C_P)}{(-S)(V(1-T\alpha)) - (V)(C_P)} \\ &= \frac{\frac{C_P}{T}(1-T\alpha) + \alpha C_P}{-S(1-T\alpha) - C_P} = \frac{C_P \left( \frac{1}{T} - \alpha + \alpha \right)}{-S(1-T\alpha) - C_P} \\ \left( \frac{\partial S}{\partial G} \right)_H &= \frac{-C_P}{TS(1-T\alpha) + TC_P} \quad (2) \end{aligned}$$

$$\left( \frac{\partial S}{\partial H} \right)_G = \frac{\begin{vmatrix} S_T & G_T \\ S_P & G_P \end{vmatrix}}{\begin{vmatrix} H_T & G_T \\ H_P & G_P \end{vmatrix}} = \frac{S_T G_P - S_P G_T}{H_T G_P - H_P G_T}$$

$$\begin{aligned} \left( \frac{\partial S}{\partial H} \right)_G &= \frac{\left( \frac{C_P}{T} \right) (V) - (-V\alpha)(-S)}{(V)(C_P) - (-S)(V(1-T\alpha))} \\ \left( \frac{\partial S}{\partial H} \right)_G &= \frac{C_P - T\alpha S}{TS(1-T\alpha) + TC_P} \quad (3) \end{aligned}$$

### Problem 5 (10 points)

This problem has 3 parts. Answer all parts.

#### **(Part 1)** (4 points)

Using the combined 1<sup>st</sup> and 2<sup>nd</sup> laws,  $dU = T dS - P dV$ , the definition of

$C_V$  and the Maxwell relation,  $\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$ , prove the following

thermodynamic relation (where familiar notation is used):

$$dU = C_V dT + \left[ T \left( \frac{\partial P}{\partial T} \right)_V - P \right] dV \rightarrow \text{(Equation 1)}$$

$$dU = T \left[ \left( \frac{\partial S}{\partial T} \right)_V dT + \left( \frac{\partial S}{\partial V} \right)_T dV \right] - P dV = T \left( \frac{\partial S}{\partial T} \right)_V dT + \left[ T \left( \frac{\partial S}{\partial V} \right)_T - P \right] dV$$

or using the definitions of  $C_V$  and the given Maxwell equation:

$$dU = C_V dT + \left[ T \left( \frac{\partial P}{\partial T} \right)_V - P \right] dV$$

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**(Part 2) (3 points)**

Applying the concept of exact differential to Equation 1

show that:  $\left(\frac{\partial C_v}{\partial v}\right)_T = T \left(\frac{\partial^2 P}{\partial T^2}\right)_v \rightarrow \text{(Equation 2)}$

**(Part 2)**

Applying the test for exactness of the differential in **Equation (1)** above, we see that

$$\left(\frac{\partial C_v}{\partial v}\right)_T = \left(\frac{\partial \left(T \left(\frac{\partial P}{\partial T}\right)_v - P\right)}{\partial T}\right)_v \Rightarrow \left(\frac{\partial C_v}{\partial v}\right)_T = T \left(\frac{\partial^2 P}{\partial T^2}\right)_v + \left(\frac{\partial P}{\partial T}\right)_v - \left(\frac{\partial P}{\partial T}\right)_v$$

or  $\left(\frac{\partial C_v}{\partial v}\right)_T = T \left(\frac{\partial^2 P}{\partial T^2}\right)_v$ . Hence proved.

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**(Part 3) (3 points)**

We have used in many occasions in this course that the specific energy  $U$  of an ideal gas is only a function of temperature  $T$ . Prove that this is indeed the case starting from Equations (1) and (2) above and using  $PV=RT$  for an ideal gas.

$$dU = C_v dT + \left[ T \left( \frac{\partial P}{\partial T} \right)_V - P \right] dV$$

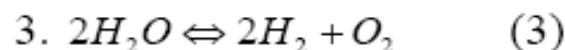
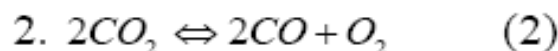
$$\left( \frac{\partial C_v}{\partial V} \right)_T = T \left( \frac{\partial^2 P}{\partial T^2} \right)_V \Rightarrow \text{for an ideal gas} \Rightarrow \left( \frac{\partial C_v}{\partial v} \right)_T = 0. \text{ Thus } C_v \text{ is}$$

independent of  $V$ .

$$dU = C_v dT + \left[ T \left( \frac{\partial P}{\partial T} \right)_V - P \right] dv = C_v dT + \left[ T \frac{R}{V} - P \right] dV = C_v dT + [P - P] dV$$

### Problem 6 (10 points)

Consider the following reactions



Show that the equilibrium constants are related by the

expression  $K_1 = \left(\frac{K_3}{K_2}\right)^{1/2}$ . Assume ideal gas behavior and a temperature of T.

$$\left(\Delta G^\circ\right)_{(1)} = \bar{g}_{\text{H}_2}^\circ + \bar{g}_{\text{CO}_2}^\circ - \bar{g}_{\text{CO}}^\circ - \bar{g}_{\text{H}_2\text{O}}^\circ$$

$$\left(\Delta G^\circ\right)_{(2)} = 2\bar{g}_{\text{CO}}^\circ + \bar{g}_{\text{O}_2}^\circ - 2\bar{g}_{\text{CO}_2}^\circ$$

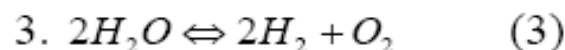
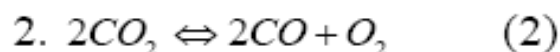
$$\left(\Delta G^\circ\right)_{(3)} = 2\bar{g}_{\text{H}_2}^\circ + \bar{g}_{\text{O}_2}^\circ - 2\bar{g}_{\text{H}_2\text{O}}^\circ$$

From inspection, by combining reactions, it is evident that

$$\left(\Delta G^\circ\right)_{(1)} = \frac{1}{2} \left[ \left(\Delta G^\circ\right)_{(3)} - \left(\Delta G^\circ\right)_{(2)} \right]$$

## Problem 6 (10 points)

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Show that the equilibrium constants are related by the

expression  $K_1 = \left(\frac{K_3}{K_2}\right)^{1/2}$ . Assume ideal gas behavior and a temperature of T.

$$(\Delta G^\circ)_{(1)} = \frac{1}{2} [(\Delta G^\circ)_{(3)} - (\Delta G^\circ)_{(2)}]$$

Using  $\ln K = -\frac{\Delta G^\circ}{RT}$  this becomes:

$$\ln K_1 = \frac{1}{2} [\ln K_3 - \ln K_2]$$

This can then be reduced to:

$$K_1 = \left(\frac{K_3}{K_2}\right)^{1/2}$$