

CHAPTER 5: THE SECOND LAW OF THERMODYNAMICS

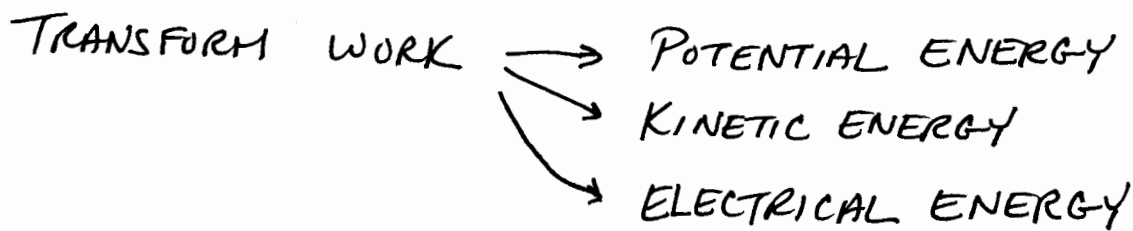
RECALL FIRST LAW:

CONSERVATION OF ENERGY

BUT, THERE ARE RESTRICTIONS ON THE DIRECTION OF ENERGY TRANSFER.

WHY? TWO FORMS OF ENERGY

HEAT + WORK



IF NO FRICTION... THEN $\eta = 100\%$

How ABOUT HEAT?

WHEN TRANSFORMING HEAT TO WORK,

$$\eta \leq 40\% \quad \underline{\underline{\text{(REALITY)}}}$$

(MECHANICAL + ELECTRICAL ENERGY)

WE ALSO KNOW FROM EXPERIENCE THAT HEAT FLOWS FROM A HOTTER TO COOLER BODY. (NEVER IN THE OTHER DIRECTION.)

5.1 STATEMENTS OF THE SECOND LAW.

STATEMENT #1: "NO APPARATUS CAN OPERATE IN SUCH A WAY THAT ITS ONLY EFFECT (IN SYSTEM AND SURROUNDINGS) IS TO CONVERT HEAT ABSORBED BY A SYSTEM COMPLETELY INTO WORK DONE BY THE SYSTEM."

STATEMENT #2: "NO PROCESS IS POSSIBLE WHICH CONSISTS SOLELY IN THE TRANSFER OF HEAT FROM ONE TEMPERATURE TO A HIGHER ONE."

WHY IS THIS IMPORTANT?

CONSIDER HOW WE PRODUCE ELECTRICITY.

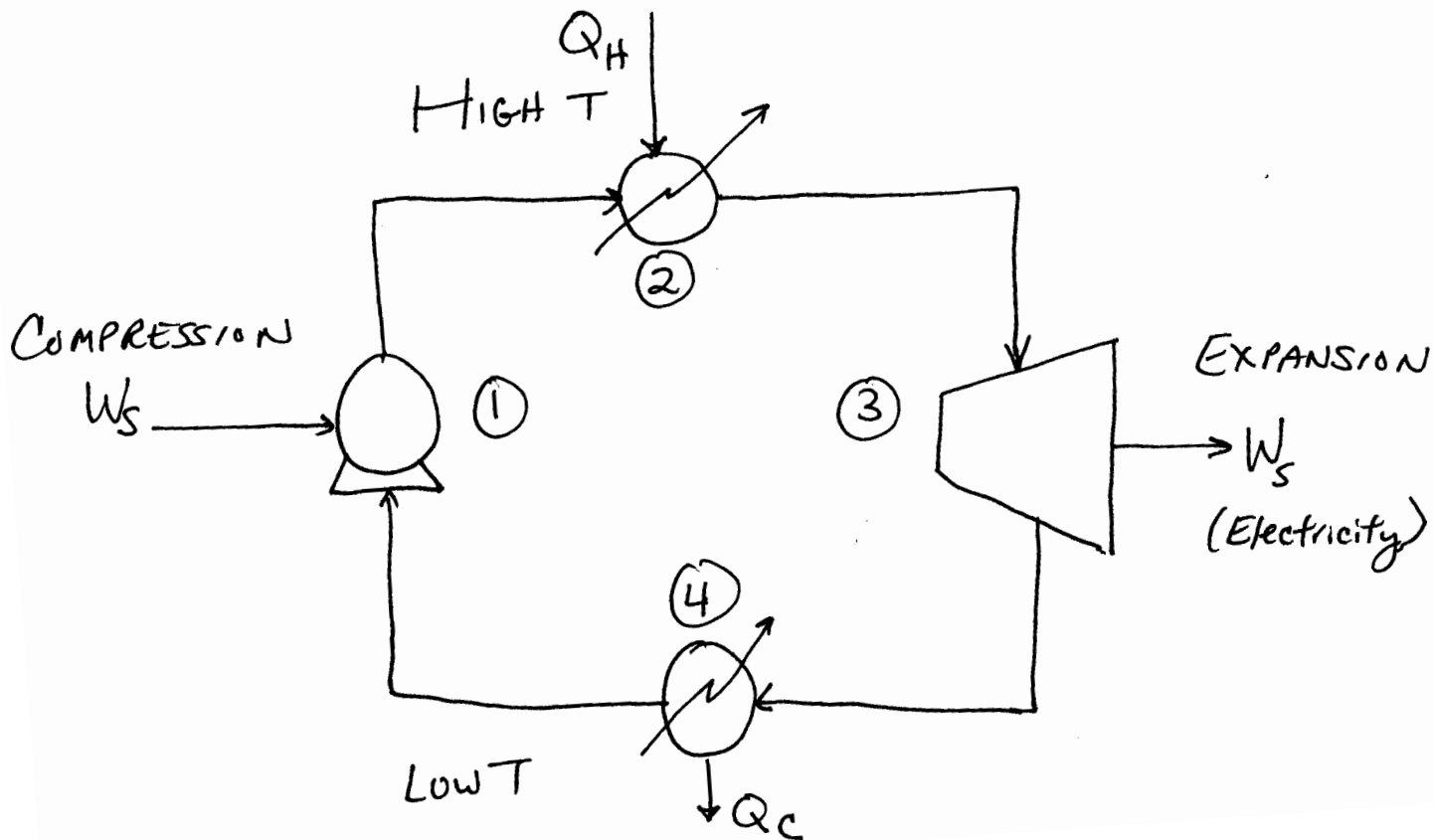
HEAT \rightarrow WORK \rightarrow ELECTRICITY

So \nearrow LOW IS A REAL PROBLEM.

5.2 HEAT ENGINES

\Rightarrow A DEVICE THAT PRODUCES WORK FROM HEAT IN A CYCLIC PROCESS.

EXAMPLE: STEAM POWER PLANT



STEP 1:

PUMPING LIQ. WATER TO HIGH PRESSURE BOILER.

STEP 2:

$\Delta H_{\text{COMBUSTION}}$ TRANSFERRED TO BOILER WATER.
 CONVERT TO HIGH P, HIGH T STEAM.

STEP 3:

HEAT CONVERTED TO WORK IN TURBINE,
 EXPANSION OF STEAM TO REDUCED P & T.

STEP 4:

CONDENSE EXHAUST TURBINE STEAM,
 REMOVE HEAT + TRANSFER TO SURROUNDINGS.

SO, HEAT ABSORPTION AT HIGH T = $|Q_H|$

HEAT REJECTED AT LOW T = $|Q_C|$

PRODUCTION OF WORK = $|W|$

1ST LAW: $|W| = |Q_H| - |Q_C|$

⇒ EFFICIENCY

$$\eta \equiv \frac{|W|}{|Q_H|} = \frac{|Q_H| - |Q_C|}{|Q_H|} = 1 - \frac{|Q_C|}{|Q_H|}$$

ONLY WAY FOR $\eta=1$ IS FOR $|Q_C| \rightarrow 0$.

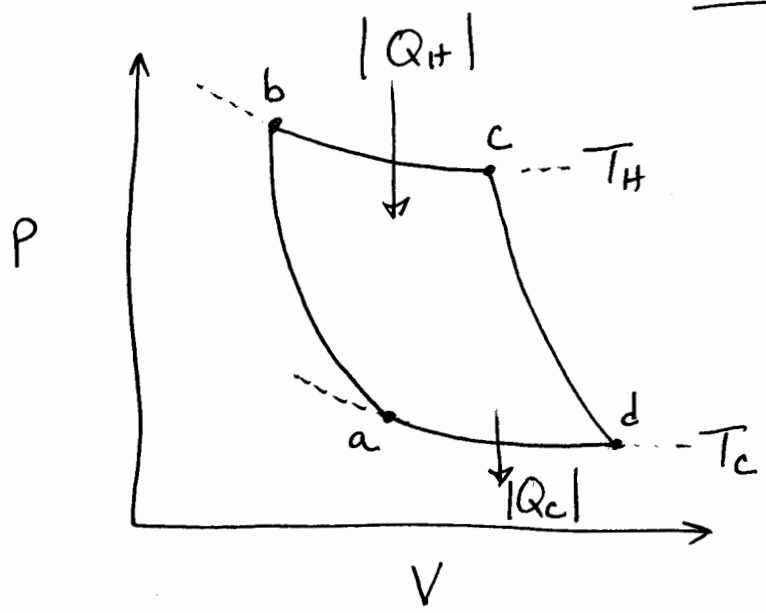
EQUIPMENT LIKE THIS HAS NEVER BEEN MADE.

⇒ BASIS FOR STATEMENT #1.

⇒ $\eta = 100\%$. NOT POSSIBLE.

→ WHAT IS THE UPPER LIMIT?

MAKE REVERSIBLE ⇒ CARNOT ENGINE



FOR IDEAL GAS

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a → b: ADIABATIC COMPRESSION ($T_C \rightarrow T_H$)

b → c: ISOTHERMAL EXPANSION (w/ ABSORPTION OF $|Q_H|$)

c → d: ADIABATIC EXPANSION ($T_H \rightarrow T_C$)

d → a: ISOTHERMAL COMPRESSION (w/ REJECTION OF $|Q_C|$)

FIRST LAW STILL HOLDS:

$$|W| = \underbrace{|Q_H|}_{\text{from isothermal expansion}} - \underbrace{|Q_C|}_{\text{from isothermal compression}}$$

FIRST, LOOK AT ISOTHERMAL STEPS:

$$Q = RT \ln \frac{V_2}{V_1} = -RT \ln \frac{P_2}{P_1}$$

$$\text{So, } Q_H = RT_H \ln \frac{V_c}{V_b} = |Q_H|$$

(HEAT ABSORBED BY SYSTEM)

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$$\text{AND, } Q_c = RT_c \ln \frac{V_a}{V_d}$$

$$\text{but, } \frac{V_a}{V_d} < 1 \Rightarrow \ln \frac{V_a}{V_d} < 0$$

$$\text{So, } Q_c = -RT_c \ln \frac{V_d}{V_a}$$

$$\text{AND, } |Q_c| = RT_c \ln \frac{V_d}{V_a}$$

THEREFORE,

$$\frac{|Q_H|}{|Q_C|} = \frac{RT_H \ln(V_c/V_b)}{RT_C \ln(V_d/V_a)}$$

NEXT, LOOK AT ADIABATIC PROCESSES:

$$dQ = 0$$

$$\frac{dT}{T} = -\frac{R}{C_V} \frac{dV}{V}$$

$$\int_{T_c}^{T_H} -\frac{C_v}{R} \frac{dT}{T} = \int_{V_a}^{V_b} \frac{dV}{V} = \ln \frac{V_b}{V_a} = -\ln \frac{V_a}{V_b}$$

$$\text{So, } \boxed{\int_{T_c}^{T_H} \frac{C_v}{R} \frac{dT}{T} = \ln \frac{V_a}{V_b}} \quad \underline{\underline{a \rightarrow b}}$$

$$\int_{T_H}^{T_c} -\frac{C_v}{R} \frac{dT}{T} = \int_{V_c}^{V_d} \frac{dV}{V} = \ln \frac{V_d}{V_c}$$

$$\boxed{\int_{T_c}^{T_H} \frac{C_v}{R} \frac{dT}{T} = \ln \frac{V_d}{V_c}} \quad \underline{\underline{c \rightarrow d}}$$

NOTICE: LHS ON BOTH IS THE SAME, SO...

$$\ln \left(\frac{V_a}{V_b} \right) = \ln \left(\frac{V_d}{V_c} \right)$$

$$\text{Recall } \frac{|Q_H|}{|Q_C|} = \frac{T_H}{T_c} \boxed{\frac{\ln(V_c/V_b)}{\ln(V_d/V_a)}} \quad \leftarrow \text{LOOKING FOR HELP HERE...}$$

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$$\ln\left(\frac{V_a}{V_b}\right) = \ln\left(\frac{V_d}{V_c}\right)$$

$$\Rightarrow \frac{V_a}{V_b} = \frac{V_d}{V_c}$$

Multiply each
side by $\frac{V_c}{V_a}$

$$\frac{V_c}{V_a} \frac{V_a}{V_b} = \frac{V_c}{V_a} \frac{V_d}{V_c}$$

$$\frac{V_c}{V_b} = \frac{V_d}{V_a} \Rightarrow \ln\left(\frac{V_c}{V_b}\right) = \ln\left(\frac{V_d}{V_a}\right)$$

$$\Rightarrow \boxed{\frac{\ln(V_c/V_b)}{\ln(V_d/V_a)} = 1}$$

SUBSTITUTE

$$\Rightarrow \boxed{\frac{|Q_H|}{|Q_C|} = \frac{T_H}{T_C}} \quad \textcircled{1}$$

Now, BACK TO EFFICIENCY

$$\eta = \frac{|W|}{|Q_H|} = 1 - \frac{|Q_C|}{|Q_H|} = \boxed{1 - \frac{T_C}{T_H} = \eta} \quad (2)$$

EQUATIONS (1) + (2) ARE CARNOT'S EQUATIONS.

$$\begin{aligned} \text{TO GET } \eta = 1, \quad T_C &\rightarrow 0 \text{ K} \\ &\text{or} \\ T_H &\rightarrow \infty \end{aligned}$$

NOT PRACTICAL ON EARTH.

COOLING WATER ($\sim 300 \text{ K}$)

FURNACE ($\sim 600 \text{ K}$)

$$\Rightarrow \eta = 1 - \frac{300 \text{ K}}{600 \text{ K}} = 0.5 \quad (\text{CARNOT})$$

ACTUAL ≈ 0.35 or 35%

EXAMPLE 5.1 800,000 KW Plant = |W|

GENERATE STEAM @ 585K

REJECT HEAT @ 295 K

IF $\eta = 0.70$ OF MAX VALUE, HOW MUCH HEAT IS REJECTED TO RIVER?

$$\eta_{\text{max}} = 1 - \frac{295\text{K}}{585\text{K}} = 0.4957$$

$$\eta = 0.7 \eta_{\text{max}} = 0.7(0.4957) = 0.347$$

REST OF HEAT LOST TO RIVER.

$$|W| = |Q_H| - \underbrace{|Q_c|}_{\text{HEAT LOST TO RIVER}}$$

$$\eta = 1 - \frac{|Q_c|}{|Q_H|} = 1 - \frac{|Q_c|}{|W| + |Q_c|}$$

$$\eta = \frac{|W| + \cancel{|Q_c|} - \cancel{|Q_c|}}{|W| + |Q_c|}$$

COMMON DENOMINATOR

INVERT

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$$\frac{1}{\eta} = \frac{|W| + |Q_c|}{|W|}$$

SOLVE FOR
 $|Q_c|$

$$\frac{|W|}{\eta} - |W| = |Q_c|$$

$$|Q_c| = \frac{800,000 \text{ kW}}{0.347} - 800,000 \text{ kW}$$

$$|Q_c| = 1,505,475 \text{ kW}$$

NEXT, ENTROPY!

5.4 ENTROPY

RECALL FROM CARNOT:

$$\frac{|Q_H|}{|Q_C|} = \frac{T_H}{T_C} \quad \underline{\underline{\text{or}}} \quad \frac{|Q_H|}{T_H} = \frac{|Q_C|}{T_C}$$

BY CONVENTION, HEAT ADDED TO SYSTEM $\Rightarrow (+)$
HEAT REMOVED FROM SYSTEM $\Rightarrow (-)$

\Rightarrow REMOVE ABSOLUTE VALUES.

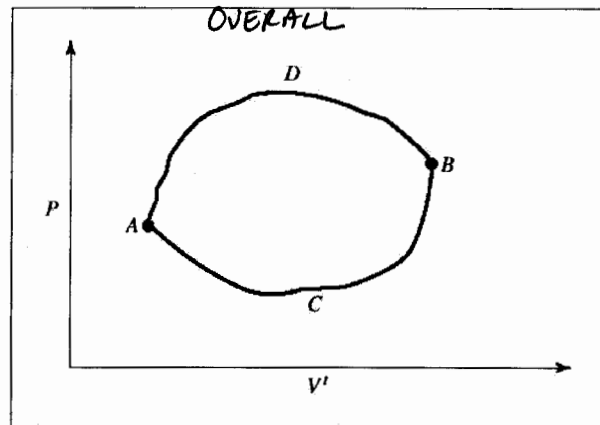
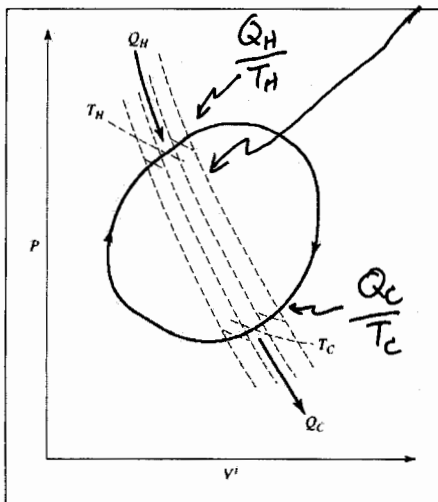
$$\frac{Q_H}{T_H} = -\frac{Q_C}{T_C} \Rightarrow \boxed{\frac{Q_H}{T_H} + \frac{Q_C}{T_C} = 0}$$

(+) (-) (-)
 (+) (+)

NOTE: $\frac{Q}{T}$

NOW, HOW DOES CARNOT APPLY TO OTHER REVERSIBLE CYCLES?

ADJACENT STEPS



COMBINE EACH SET ... VERY SMALL STEPS.

$$\underbrace{\frac{dQ_H}{T_H}}_{\text{ISOTHERMAL STEP}} + \underbrace{\frac{dQ_C}{T_C}}_{\text{ISOTHERMAL STEP}} = 0$$

ADD THEM ALL UP
(INTEGRATION)

$$\oint \frac{dQ_{REV}}{T} = 0$$

REVERSIBLE BECAUSE DIFFERENTIAL STEPS.

SUMMED UP FOR THE ENTIRE CYCLE.

NEW TERM: ENTROPY

$$dS^t = \frac{dQ_{REV}}{T} \quad \underline{\text{or}} \quad dQ_{REV} = T dS^t$$

FROM OVERALL:

POINTS A+B ARE TWO EQUILIBRIUM STATES.

PATHS ACB + ADB ARE TWO ARBITRARY PATHS FROM A → B,

$$\Delta S^t = \int_{ACB} \frac{dQ_{REV}}{T} \quad \text{and} \quad \Delta S^t = \int_{ADB} \frac{dQ_{REV}}{T}$$

IS ENTROPY A STATE FUNCTION?

$$\oint \frac{dQ_{rev}}{T} = 0$$

$$\Rightarrow \int_{ACB} \frac{dQ_{rev}}{T} - \int_{ADB} \frac{dQ_{rev}}{T} = 0$$

$$\Rightarrow \int_{ACB} \frac{dQ_{rev}}{T} = \int_{ADB} \frac{dQ_{rev}}{T} \Rightarrow \underline{\underline{YES}}, \text{ ENTROPY IS A STATE FUNCTION.}$$

What will this do for us?

FINITE VALUE OF ENTROPY AT A+B.

$$S_A^t + S_B^t$$

$$\Rightarrow \Delta S^t = S_B^t - S_A^t \quad (\text{PATH INDEPENDENT})$$

What if path is irreversible?

$$\Delta S^t = S_B^t - S_A^t \quad (\text{STILL HOLDS})$$

HOWEVER, $\Delta S^t \neq \int \frac{dQ}{T}$ ← IRREVERSIBLE.

RATHER, CHOOSE REVERSIBLE PATH, SAME ENDPOINTS.

then, $\Delta S^t = \int \frac{dQ_{rev}}{T}$ (OK, because state function)

5.5 ENTROPY CHANGES OF AN IDEAL GAS

RECALL FIRST LAW:

$$dU = dQ_{rev} - \underbrace{PdV}_{dw}$$

ENTHALPY:

$$H = U + PV$$

$$dH = dU + PdV + VdP$$

↑
substitute

$$dH = dQ_{rev} - \cancel{PdV} + \cancel{PdV} + VdP$$

$$\Rightarrow dQ_{rev} = dH - VdP$$

IDEAL GAS: $PV = RT$ + $dH = C_p^{ig} dT$

$$\frac{1}{T} (dQ_{rev}) = \frac{1}{T} \left(C_p^{ig} dT - \frac{RT}{P} dP \right)$$

$$\frac{dQ_{rev}}{T} = C_p^{ig} \frac{dT}{T} - R \frac{dP}{P}$$



$$\left(dS = C_p^{ig} \frac{dT}{T} - R d \ln P \right) \frac{1}{R}$$

$$\int \frac{dS}{R} = \int \frac{C_p^{ig}}{R} \frac{dT}{T} - \int d \ln P$$

$$\frac{\Delta S}{R} = \int_{T_0}^T \frac{C_p^{ig}}{R} \frac{dT}{T} - \ln \left(\frac{P}{P_0} \right) \quad \leftarrow \text{IDEAL GAS.}$$

EXAMPLE 5.3 METHANE GAS AT 550 K AND 5 BAR UNDERGOES A REVERSIBLE, ADIABATIC EXPANSION TO 1 BAR. ASSUMING CH₄ TO BE AN IDEAL GAS AT THESE CONDITIONS, FIND ITS FINAL TEMPERATURE.

REVERSIBLE, ADIABATIC EXPANSION $\Rightarrow dQ = 0$

$$\Rightarrow \Delta S = 0$$

$$\Rightarrow 0 = \int_{T_0}^T \frac{C_p^{ig}}{R} \frac{dT}{T} - \ln \left(\frac{P}{P_0} \right)$$

Where: $T = \text{unknown}$
 $T_0 = 550\text{K}$
 $P_0 = 5\text{ bar}$
 $P = 1\text{ bar}$

FROM TABLE C.1:

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$A = 1.702$
 $B = 9.081 \times 10^{-3}$
 $C = -2.164 \times 10^{-6}$

$$\Rightarrow \frac{C_p^{ig}}{R} = 1.702 + (9.081 \times 10^{-3})T + (-2.164 \times 10^{-6})T^2$$

PLUG + CHUG

$$0 = \int_{550}^T \left[1.702 + 9.081 \times 10^{-3}T - 2.164 \times 10^{-6}T^2 \right] \frac{dT}{T} - \ln\left(\frac{P}{P_0}\right)$$

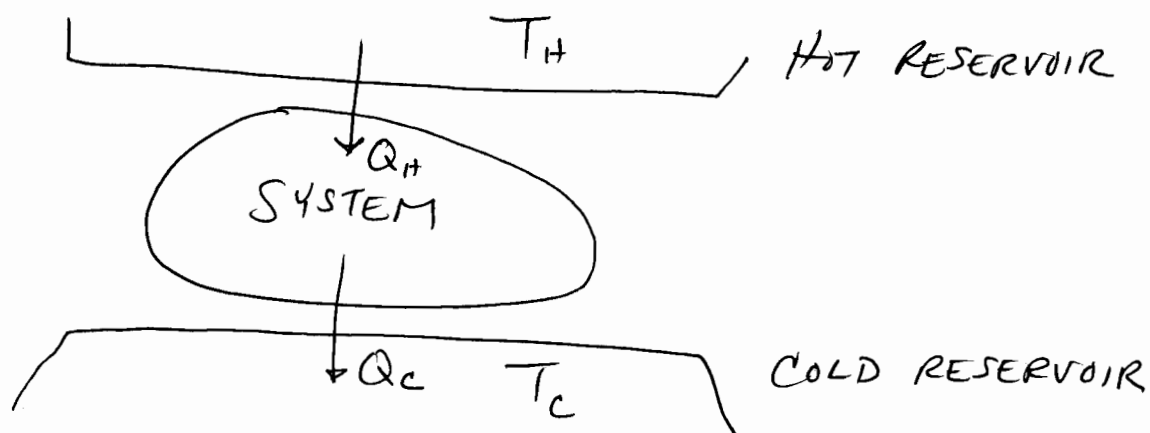
$$0 = \int_{550}^T \frac{1.702}{T} dT + \int_{550}^T 9.081 \times 10^{-3} dT - \int_{550}^T 2.164 \times 10^{-6} T dT - \ln\left(\frac{P}{P_0}\right)$$

$$0 = 1.702 (\ln T) \Big|_{550}^T + 9.081 \times 10^{-3} T \Big|_{550}^T - \frac{2.164 \times 10^{-6}}{2} T^2 \Big|_{550}^T - \ln\left(\frac{1}{5}\right)$$

$$0 = 1.702 \ln\left(\frac{T}{550}\right) + 9.081 \times 10^{-3} (T - 550) - 1.082 \times 10^{-6} (T^2 - 550^2)$$

$$- \ln\left(\frac{1}{5}\right) \Rightarrow \text{SOLVER: } \boxed{T = 411.3\text{K}}$$

5.6 MATHEMATICAL STATEMENTS OF SECOND LAW.



ENTROPY CHANGES OF HEAT RESERVOIRS.

HOT: $\Delta S_H^t = \frac{-|Q|}{T_H}$

COLD: $\Delta S_C^t = \frac{|Q|}{T_C}$

$$\Delta S_{TOTAL} = \Delta S_H^t + \Delta S_C^t = \frac{-|Q|}{T_H} + \frac{|Q|}{T_C}$$

$$\Delta S_{TOTAL} = |Q| \frac{(-T_C + T_H)}{T_H T_C} = |Q| \frac{(T_H - T_C)}{T_H T_C}$$

$$(+)$$

$$\frac{(T_H - T_C)}{(+)(+)}$$

SIGN? $T_H > T_C$

$$\Rightarrow \boxed{\Delta S_{TOTAL} \geq 0}$$

NOTE: SYSTEM IS COMPLETE CYCLE

$$\Rightarrow \Delta S_{\text{SYSTEM}} = 0$$

$$\Rightarrow \Delta S_{\text{TOTAL}} \geq 0$$

(AND BASED ON SURROUNDINGS)

$$\Delta S_{\text{total}} = \frac{-|Q_H|}{T_H} + \frac{|Q_C|}{T_C}$$

Recall, $|W| = |Q_H| - |Q_C|$ (First Law)

COMBINE TO ELIMINATE $|Q_C|$ + SOLVE FOR $|W|$,

$$\Delta S_{\text{TOTAL}} = \frac{-|Q_H|}{T_H} + \frac{1}{T_C} (|Q_H| - |W|)$$

$$\Delta S_{\text{TOTAL}} = \frac{-|Q_H|}{T_H} + \frac{|Q_H|}{T_C} - \frac{|W|}{T_C}$$

$$\frac{|W|}{T_C} = -\Delta S_{\text{TOTAL}} + |Q_H| \left(\frac{-T_C + T_H}{T_H T_C} \right)$$

$$|W| = -T_C \Delta S_{\text{TOTAL}} + |Q_H| \left(1 - \frac{T_C}{T_H} \right)$$

$$|W|_{\max} = |Q_H| \left(1 - \frac{T_C}{T_H} \right)$$

CARNOT
 $\Delta S_{\text{TOTAL}} = 0$

EXAMPLE 5.4

A 40-KG STEEL CASTING ($C_p = 0.5 \text{ KJ} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$) AT A TEMPERATURE OF 450°C IS QUENCHED IN 150 KG OF OIL ($C_p = 2.5 \text{ KJ} / \text{kg} \cdot \text{K}$) @ 25°C . IF THERE ARE NO HEAT LOSSES, WHAT IS THE CHANGE IN ENTROPY OF (a) THE CASTING, (b) THE OIL, AND (c) BOTH CONSIDERED TOGETHER?

FIRST LAW

$$0 = (40 \text{ kg}) \left(\frac{0.5 \text{ KJ}}{\text{kg} \cdot \text{K}} \right) (T - 450^\circ\text{C}) + (150 \text{ kg}) \left(\frac{2.5 \text{ KJ}}{\text{kg} \cdot \text{K}} \right) (T - 25^\circ\text{C})$$

$$\Rightarrow T = 46.5^\circ\text{C}$$

Sensible Heat

$$dQ_{\text{rev}} = dH = C_p dT$$

(a) ΔS^t (casting)

$$= m \int \frac{C_p dT}{T} = m C_p \ln \left(\frac{T_2}{T_1} \right)$$

$$= 40 \text{ kg} \left| \frac{0.5 \text{ KJ}}{\text{kg} \cdot \text{K}} \right| \ln \left(\frac{273.15 + 46.52^\circ\text{C}}{273.15 + 450^\circ\text{C}} \right) = -16.32 \frac{\text{KJ}}{\text{K}}$$

(b) $\Delta S^t(\text{oil})$

$$= 150 \text{ Kg} \left| \frac{2.5 \text{ kJ}}{\text{kg} \cdot \text{K}} \ln \left(\frac{273.15 + 46.52}{273.15 + 25} \right) \right. = 26.13 \frac{\text{kJ}}{\text{K}}$$

(c) $\Delta S_{\text{total}} = -16.33 \frac{\text{kJ}}{\text{K}} + 26.13 \frac{\text{kJ}}{\text{K}}$

$$\Delta S_{\text{TOTAL}} = 9.80 \frac{\text{kJ}}{\text{K}}$$

NEXT, OPEN SYSTEMS.

5.7 ENTROPY BALANCE FOR OPEN SYSTEMS

⇒ ENTROPY IS NOT CONSERVED

$$\underbrace{\Delta(Sm)_{fs}}_{\substack{\text{NET CHANGE} \\ \text{FLOWING} \\ \text{STREAMS}}} + \underbrace{\frac{d(MS)_{cv}}{dt}}_{\substack{\text{RATE OF CHANGE} \\ \text{IN CONTROL} \\ \text{VOLUME}}} + \underbrace{\frac{dS_{surr}^t}{dt}}_{\substack{\text{RATE OF} \\ \text{CHANGE} \\ \text{IN} \\ \text{SURROUNDINGS}}} = \underbrace{\dot{S}_G}_{\substack{\text{ENTROPY} \\ \text{GENERATED}}} \geq 0$$

↑
Put in terms of Q

$$\Delta(Sm)_{fs} + \frac{d(MS)_{cv}}{dt} - \sum_j \frac{\dot{Q}_j}{T_{\sigma,j}} = \dot{S}_G \geq 0$$

where $j \equiv$ FOR EACH SURROUNDING

$T_{\sigma,j} \equiv$ TEMPERATURE OF SURROUNDING j

$\dot{S}_G = 0$ ONLY FOR COMPLETELY REVERSIBLE.

⇒ INTERNAL REVERSIBLE

⇒ HEAT TRANSFER TO SURROUNDING ALSO REVERSIBLE,

IF STEADY STATE FLOW, $(m\dot{s})_{cv} = \text{constant}$

$$\Rightarrow \frac{d(m\dot{s})_{cv}}{dt} = 0$$

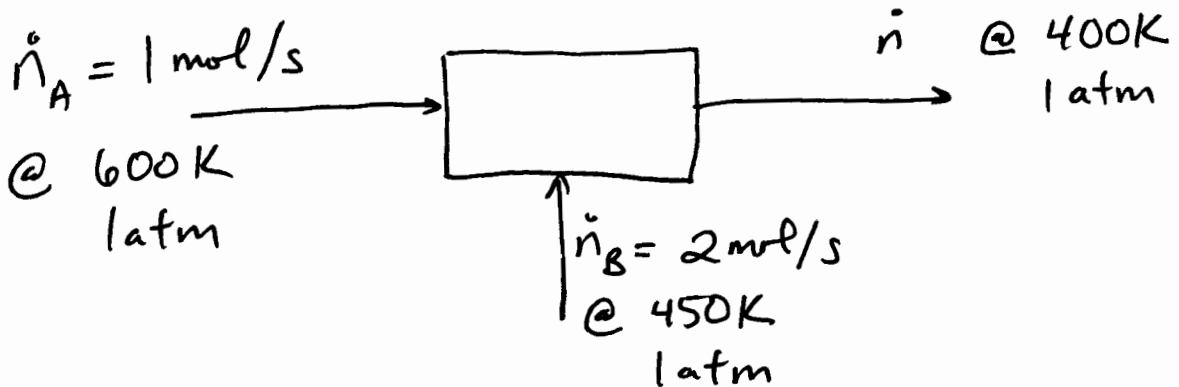
AND, IF ONLY ONE ENTRANCE & EXIT (w/ SAME in)

$$\Delta S - \sum_j \frac{Q_j}{T_{0,j}} = S_G \geq 0$$

← FOR UNIT AMOUNT OF FLUID MOVING THRU SYSTEM.

EXAMPLE 5.5

In a steady-state flow process, 1 mol s⁻¹ of air at 600 K and 1 atm is continuously mixed with 2 mol s⁻¹ of air at 450 K and 1 atm. The product stream is at 400 K and 1 atm. A schematic representation of the process is shown in Fig. 5.7. Determine the rate of heat transfer and the rate of entropy generation for the process. Assume that air is an ideal gas with $C_p = (7/2)R$, that the surroundings are at 300 K, and that kinetic- and potential-energy changes are negligible.



$\dot{Q} = ?$ $\dot{S}_G = ?$

FIRST LAW: (OPEN SYSTEM) $\Delta \left[(H + \frac{1}{2}u^2 + zg)n \right]_{fs} = \dot{Q} + \dot{W}_S$

$$\text{If } \Delta E_k, \Delta E_p, \dot{W}_s = 0$$

$$\Delta [H \dot{n}]_{fs} = \dot{Q}$$

$$\Rightarrow \dot{Q} = \underbrace{\dot{n} H}_{\text{OUT}} - \underbrace{(\dot{n}_A H_A + \dot{n}_B H_B)}_{\text{IN}}$$

$$= (\dot{n}_A + \dot{n}_B) H - \dot{n}_A H_A - \dot{n}_B H_B$$

$$= \dot{n}_A \underbrace{(H - H_A)}_{\Delta H} + \dot{n}_B \underbrace{(H - H_B)}_{\Delta H}$$

IDEAL GAS:

$$\Delta H = c_p \Delta T \quad \text{w/ } c_p = \frac{7}{2} R$$

$$\underline{\text{So:}} \quad \dot{Q} = \dot{n}_A c_p (T - T_A) + \dot{n}_B c_p (T - T_B)$$

PLUG + CHUG:

$$\dot{Q} = \frac{1 \text{ mol}}{\text{s}} \left| \frac{7}{2} \right| \frac{8.314 \text{ J}}{\text{mol} \cdot \text{K}} (400 \text{ K} - 600 \text{ K})$$

$$+ 2 \frac{\text{ mol}}{\text{ s}} \left| \frac{7}{2} \right| \frac{8.314 \text{ J}}{\text{ mol} \cdot \text{K}} (400 \text{ K} - 450 \text{ K})$$

$$\Rightarrow \boxed{\dot{Q} = -8,729.7 \frac{\text{J}}{\text{s}}}$$

Next, Entropy:

$$\Delta(Si)_{fs} - \sum_j \frac{\dot{Q}_j}{T_{\sigma,j}} = \dot{S}_G$$

$$\dot{S}_G = \underbrace{\dot{n} S}_{\text{OUT}} - \underbrace{(\dot{n}_A S_A + \dot{n}_B S_B)}_{\text{IN}} - \frac{\dot{Q}}{T_\sigma}$$

$$= (\dot{n}_A + \dot{n}_B) S - \dot{n}_A S_A - \dot{n}_B S_B - \frac{\dot{Q}}{T_\sigma}$$

$$= \dot{n}_A (S - S_A) + \dot{n}_B (S - S_B) - \frac{\dot{Q}}{T_\sigma}$$

$$= \dot{n}_A \int_{T_A}^T \frac{C_p dT}{T} + \dot{n}_B \int_{T_B}^T \frac{C_p dT}{T} - \frac{\dot{Q}}{T_\sigma}$$

Ideal Gas w/ $C_p = \frac{7}{2} R$

$$\stackrel{\text{So}}{=} \dot{S}_G = \dot{n}_A C_p \ln\left(\frac{T}{T_A}\right) + \dot{n}_B C_p \ln\left(\frac{T}{T_B}\right) - \frac{\dot{Q}}{T_\sigma}$$

PLUG + CHUG:

$$\dot{S}_G = \left(1 \frac{\text{mol}}{\text{s}}\right) \frac{7}{2} \left| \frac{8.314 \text{ J}}{\text{mol} \cdot \text{K}} \ln\left(\frac{400}{600}\right) \right.$$

$$\left. + \left(2 \frac{\text{mol}}{\text{s}}\right) \frac{7}{2} \left| \frac{8.314 \text{ J}}{\text{mol} \cdot \text{K}} \ln\left(\frac{400}{450}\right) \right. - \left(-8,729.7 \frac{\text{J}}{\text{s}} \right) \frac{1}{300 \text{ K}} \right.$$

$$\Rightarrow \dot{S}_G = 10.45 \frac{\text{J}}{\text{s}\cdot\text{K}} \leftarrow \text{NOTE: } \dot{S}_G \geq 0 \quad \checkmark$$

5.8 CALCULATION OF IDEAL WORK

\Rightarrow KNOWING YOUR LIMITS...

When completely reversible, $\dot{S}_G = 0$

$$\Rightarrow \Delta(Sm)_{fs} - \frac{\dot{Q}}{T_\sigma} = 0$$

or

$$\dot{Q} = T_\sigma \Delta(Sm)_{fs}$$

Substitute into First Law for Flowing System...

$$\Delta \left[(H + \frac{1}{2}u^2 + zg)_{in} \right]_{fs} = T_\sigma \Delta(Sm)_{fs} + \underbrace{\dot{W}_{S(REV)}}_{\text{IDEAL WORK}}$$

Solve for \dot{W}_{IDEAL} w/ $\Delta E_k + \Delta E_p \approx 0$

$$\Rightarrow \dot{W}_{IDEAL} = \Delta(Hm)_{fs} - T_\sigma \Delta(Sm)_{fs}$$

If Single Stream In+Out of Control Volume...

$$\dot{W}_{\text{IDEAL}} = \dot{m} (\Delta H - T_{\sigma} \Delta S)$$

AND

$$W_{\text{IDEAL}} = \Delta H - T_{\sigma} \Delta S$$

BOTH FOR
COMPLETELY
REVERSIBLE

⇒ BEST CASE
(IDEAL WORK)

⇒ EFFICIENCY :

$$\eta_t \text{ (WORK REQUIRED)} = \frac{\dot{W}_{\text{IDEAL}}}{\dot{W}_s}$$

$$\eta_t \text{ (WORK PRODUCED)} = \frac{\dot{W}_s}{\dot{W}_{\text{IDEAL}}}$$

EXAMPLE 5.7

WHAT IS THE MAXIMUM WORK THAT CAN BE OBTAINED IN A STEADY STATE FLOW PROCESS FROM 1 mol N_2 (Ideal Gas) @ 800K AND 50 bar? (w/ $T_{\sigma} = 300K$ + $P_{\sigma} = 1.0133 \text{ bar}$)

MAX WORK WILL BE:

⇒ COMPLETELY REVERSIBLE PROCESS

⇒ N_2 EXITS PROCESS AT T_{σ} + P_{σ}

$$\underline{W_{IDEAL} = n \Delta H - n T_0 \Delta S}$$

ΔH: $\Delta H = \int_{T_1}^{T_2} C_p^{ig} dT$

$$\frac{C_p^{ig}}{R} = A + BT + CT^2 + \frac{D}{T^2}$$

FROM TABLE C.1: (N₂)

A = 3.280 B = 0.593 × 10⁻³ C = 0 D = 0.040 × 10⁵

$$\Delta H = R \int_{800}^{300} [3.280 + 0.593 \times 10^{-3} T + \frac{0.040 \times 10^5}{T^2}] dT$$

$$= \frac{8.314 \text{ J}}{\text{mol} \cdot \text{K}} \left[3.280(300 - 800) + \frac{0.593 \times 10^{-3}}{2} (300^2 - 800^2) - 0.040 \times 10^5 \left(\frac{1}{300} - \frac{1}{800} \right) \right]$$

⇒ $\Delta H = -15,060 \frac{\text{J}}{\text{mol}}$

ΔS: $\Delta S = R \int_{T_1}^{T_2} \frac{C_p^{ig}}{R} \frac{dT}{T} - R \ln\left(\frac{P_2}{P_1}\right)$

(30)

$$= R \int_{800}^{300} \left[\frac{3.280}{T} + 0.593 \times 10^{-3} + \frac{0.040 \times 10^5}{T^3} \right] dT - R \ln \left(\frac{1.0133}{50} \right)$$

$$= \frac{8.314 \text{ J}}{\text{mol} \cdot \text{K}} \left[3.280 \ln \left(\frac{300}{800} \right) + 0.593 \times 10^{-3} (300 - 800) \right.$$

$$\left. + 0.040 \times 10^5 \left(-\frac{1}{2} \right) \left(\frac{1}{300^2} - \frac{1}{800^2} \right) \right]$$

$$- \frac{8.314 \text{ J}}{\text{mol} \cdot \text{K}} \ln \left(\frac{1.0133}{50} \right)$$

$$\Rightarrow \boxed{\Delta S = 3.044 \frac{\text{J}}{\text{mol} \cdot \text{K}}}$$

$$\Rightarrow W_{\text{IDEAL}} = (1 \text{ mol}) \left[\frac{-15,060 \text{ J}}{\text{mol}} - 300 \text{ K} \left(\frac{3.044 \text{ J}}{\text{mol} \cdot \text{K}} \right) \right]$$

$$\Rightarrow \boxed{W_{\text{IDEAL}} = -15,973 \text{ J}} \Rightarrow \underline{\text{WORK PRODUCED}}$$

5.9 LOST WORK

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⇒ WORK LOST DUE TO IRREVERSIBILITIES
IN A PROCESS

$$\Rightarrow W_{\text{LOST}} \equiv W_S - W_{\text{IDEAL}}$$

or

$$\dot{W}_{\text{LOST}} \equiv \dot{W}_S - \dot{W}_{\text{IDEAL}}$$

where,

$$\dot{W}_S = \Delta \left[\left(H + \frac{1}{2} u^2 + z g \right) \dot{m} \right]_{fs} - \dot{Q}$$

$$\dot{W}_{\text{IDEAL}} = \Delta \left[\left(H + \frac{1}{2} u^2 + z g \right) \dot{m} \right]_{fs} - T_\sigma \Delta (S \dot{m})_{fs}$$

$$\Rightarrow \dot{W}_{\text{LOST}} = -\dot{Q} + T_\sigma \Delta (S \dot{m})_{fs}$$

Recall: (for single T_σ)

$$\Delta (S \dot{m})_{fs} - \frac{\dot{Q}}{T_\sigma} = \dot{S}_G \geq 0$$

$$\Rightarrow T_\sigma \Delta (S \dot{m})_{fs} - \dot{Q} = T_\sigma \dot{S}_G$$

$$\Rightarrow \dot{W}_{\text{LOST}} = T_\sigma \dot{S}_G$$

SINCE $\dot{S}_G \geq 0$, THEN $\dot{W}_{LOST} \geq 0$

IF COMPLETELY REVERSIBLE, $\dot{W}_{LOST} = 0$

WHICH MEANS...

CONSEQUENCES OF IRREVERSIBILITIES?

\Rightarrow MORE \dot{W}_{LOST}

SO, FOR SINGLE STREAM IN + OUT:

$$\dot{W}_{LOST} = \dot{m} T_0 \Delta S - \dot{Q}$$

$$W_{LOST} = T_0 \Delta S - Q$$

$$\dot{S}_G = \dot{m} \Delta S - \frac{\dot{Q}}{T_0}$$

$$S_G = \Delta S - \frac{Q}{T_0}$$

EXAMPLE 5.9

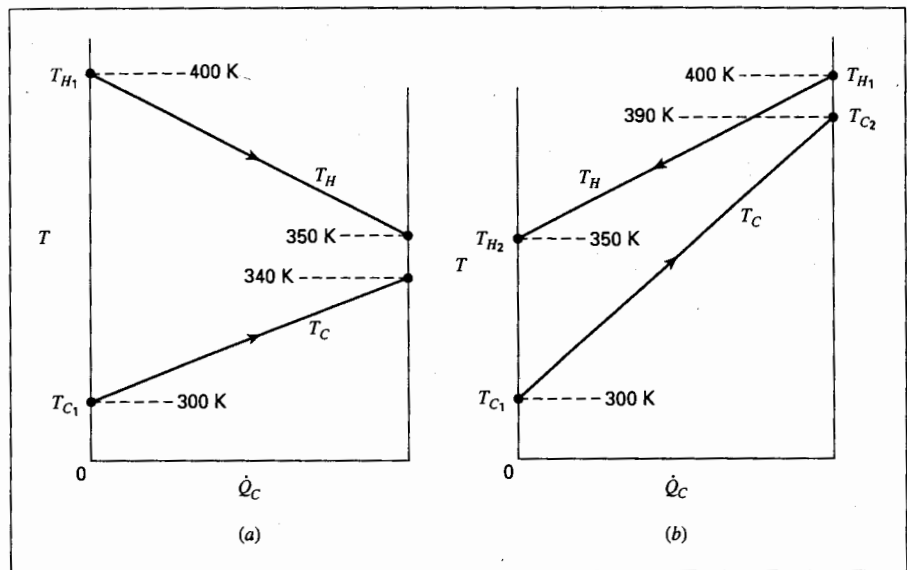


Figure 5.9: Heat exchangers. (a) Case I, cocurrent. (b) Case II, countercurrent.

$T_{H1} = 400 K$

$T_{C1} = 300 K$

$T_{H2} = 350 K$

$\dot{n}_H = 1 \frac{mol}{s}$

IDEAL GAS w/ $C_p = \frac{7}{2} R$, $T_\sigma = 300 K$

$\Delta T_{MIN} = 10 K$

$W_{LOST} = ?$ (BOTH CASES)

HEAT EXCHANGER (INSULATED)

\Rightarrow ALL Q BETWEEN STREAMS ONLY.

FIRST LAW:

$\Delta [(H + \frac{1}{2}u^2 + zg) \dot{n}]_{fs} = \dot{Q} + \dot{W}_s$

w/ $\Delta E_k, \Delta E_p, \dot{W}_s \cong 0$ ($+ \dot{Q} = 0$)

So, $\Delta [H \dot{n}]_{fs} = 0$

$\dot{n}_H (\Delta H)_H + \dot{n}_C (\Delta H)_C = 0$

$\dot{n}_H C_p (\Delta T)_H + \dot{n}_C C_p (\Delta T)_C = 0$

$\Rightarrow \frac{\dot{n}_C}{\dot{n}_H} = \frac{T_{H2} - T_{H1}}{-(T_{C2} - T_{C1})} = \frac{T_{H2} - T_{H1}}{T_{C1} - T_{C2}}$ ①

Next, Entropy:

$$\dot{S}_G = \Delta (S\dot{n})_{fs} - \cancel{\frac{\dot{Q}}{T_\sigma}}$$

$$= \dot{n}_H (\Delta S)_H + \dot{n}_C (\Delta S)_C$$

Recall $\Delta S = R \int_{T_P}^{T_2} \frac{C_p^{i2}}{R} \frac{dT}{T} - \ln\left(\frac{P_2}{P_1}\right)$

IN OUR CASE, $P_2 \approx P_1 \Rightarrow \underline{\underline{\ln(1) = 0}}$.

So,

$$\dot{S}_G = \dot{n}_H C_p \ln\left(\frac{T_{H2}}{T_{H1}}\right) + \dot{n}_C C_p \ln\left(\frac{T_{C2}}{T_{C1}}\right)$$

$$\dot{S}_G = \dot{n}_H C_p \left\{ \ln\left(\frac{T_{H2}}{T_{H1}}\right) + \frac{\dot{n}_C}{\dot{n}_H} \ln\left(\frac{T_{C2}}{T_{C1}}\right) \right\} \quad (2)$$

AND

$$\dot{W}_{\text{LOST}} = T_\sigma \dot{S}_G \quad (3)$$

APPLY EQNS. (1), (2), and (3) FOR OUR
2 CASES.

CASE 1: Cocurrent Flow. ($T_{c2} = 340K$)

① $\frac{\dot{n}_c}{\dot{n}_H} = \frac{350 - 400}{300 - 340} = 1.25$

② $\dot{S}_G = \frac{7}{2} \left| \frac{8.314 J}{mol \cdot K} \right| \frac{1 mol}{s} \left\{ \ln\left(\frac{350}{400}\right) + 1.25 \ln\left(\frac{340}{300}\right) \right\}$

$\Rightarrow \dot{S}_G = 0.667 \frac{J}{K \cdot s}$

③ $\dot{W}_{LOST} = (300K) \left(0.667 \frac{J}{K \cdot s} \right) \Rightarrow \dot{W}_{LOST} = 200.1 \frac{J}{s}$

CASE 2: Countercurrent Flow ($T_{c2} = 390K$)

① $\frac{\dot{n}_c}{\dot{n}_H} = \frac{350 - 400}{300 - 390} = 0.556$

② $\dot{S}_G = \frac{7}{2} \left| \frac{8.314 J}{mol \cdot K} \right| \frac{1 mol}{s} \left\{ \ln\left(\frac{350}{400}\right) + 0.556 \ln\left(\frac{390}{300}\right) \right\}$

$\Rightarrow \dot{S}_G = 0.359 \frac{J}{K \cdot s}$

③ $\dot{W}_{LOST} = (300K) \left(0.359 \frac{J}{K \cdot s} \right) \Rightarrow \dot{W}_{LOST} = 107.7 \frac{J}{s}$

NOTES: 1) SAME \dot{Q} ($(\Delta T)_H + \dot{n}_H$ same)

2) MUCH BETTER HEATING COUNTERCURRENT FLOW.

3) \dot{S}_G SHOWS THIS IMPROVEMENT.

\Rightarrow COUNTERCURRENT MUCH MORE EFFICIENT.