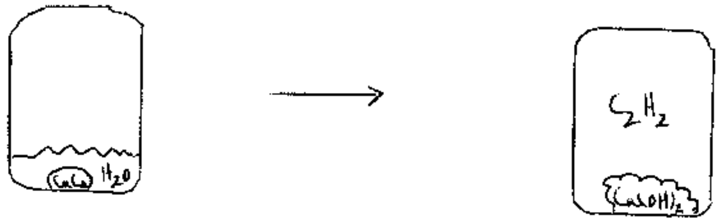
Problem Set F

Problem 20

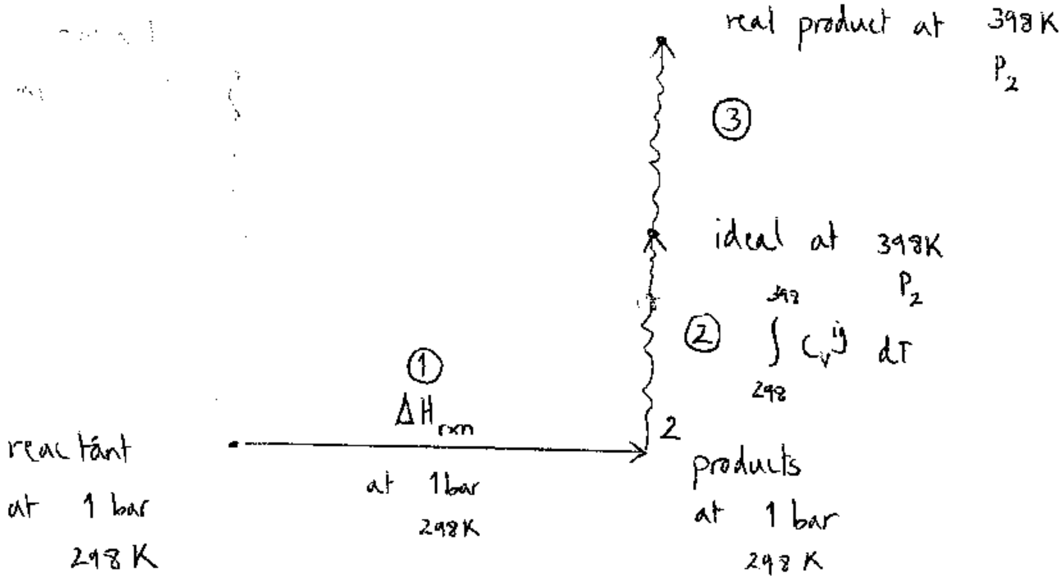
V^t 750 mL $\qquad\qquad$ $V^t = 750$ mL



$T_1 = 25°C$ $\qquad$ 125°C $\qquad$ $V_{Ca(OH)_2} = 33\ cm^3/mol$

$P_1 = 1$ bar $\qquad$ $P_2 = ?$

$$CaC_2\,(s) + 2\,H_2O\,(l) \longrightarrow C_2H_2\,(g) + Ca(OH)_2\,(s)$$



<u>Note</u>

- Reactants $CaC_2\,(s)$ and $H_2O\,(l)$ are already at standard state
- Products formed after step ① are $Ca(OH)_2\,(s)$

  $C_2H_2\,(g)$

  at standard state

Step 1

$$\Delta H_{rxn} = \Delta H^{\circ}_{f,298}(C_2H_2(g)) + \Delta H^{\circ}_{f,298}(Ca(OH)_2(s))$$

$$- \Delta H^{\circ}_{f,298}(CaC_2(s)) - 2\Delta H^{\circ}_{f,298}(H_2O(l))$$

$$= 227480 + (-986090) - (-59800) - 2(-285830)$$

$$= -127150 \text{ J/mol}$$

since we have 5 moles of $CaC_2(s)$ $\Delta H_{rxn} = -635750 \text{ J}$

Step 2

Raising T from 298 K to 398 K, at constant V $\therefore$ use ΔU

$$\Delta U = \int C_v^{ig}\, dT = \int (C_p^{ig} - R)\, dT$$

$$C_p^{ig} = C_{p,C_2H_2} + C_{p,Ca(OH)_2}$$

$$\frac{C_p^{ig}}{R} = 6.132 + 1.952\times10^{-3}\,T - 1.299\times10^{5}\,T^{-2}$$

$$+ 9.597 + 5.435\times10^{-3}\,T$$

$$C_p^{ig} = R[15.729 + 7.387\times10^{-3}\,T - 1.299\times10^{5}\,T^{-2}]$$

$$\Delta U = R\int_{298}^{398} 14.729 + 7.387\times10^{-3}\,T - 1.299\times10^{5}\,T^{-2}\, dT$$

$$= R\left[14.729\,T + 3.6935\times10^{-3}\,T^{2} + 1.299\times10^{-5}\,T^{-1}\right]_{298}^{398}$$

$$= 14383 \text{ J/mol}$$

since we will form 5 moles of C_2H_2 and $Ca(OH)_2$

$$= 71914 \quad J$$

Step 3

we know that the molar volume of $Ca(OH)_2$ (s) is $33 \ cm^3/mol$

$$\therefore \quad V^t_{Ca(OH)_2} = 5 \times 33 = 165 \ cm^3$$

$$\therefore \quad V^t_{C_2H_2} = 750 - 165 = 585 \ cm^3$$

$$\therefore \quad V_{C_2H_2} = 117 \ cm^3/mol$$

if this is an ideal gas then the pressure would be

$$P = \frac{RT}{V} = \frac{8.314 \times 398}{117 \times 10^{-6}}$$

$$= 28.3 \times 10^6 \ Pa$$

$$= 283 \ bar$$

for C_2H_2 $\quad T_c = 308.3 K \quad P_c = 61.39 \ bar \quad \omega = 0.187$

for real gas however, $\quad P = \frac{ZRT}{V}$

$\therefore$ we need to do iterative calculations

with a given P, we can calculate P_r, and T_r and hence Z from table $Z = Z^0 + \omega Z^1$ can be calculate

given Z, recalculate P using $P = \frac{ZRT}{V}$

	P	Z
1)	283 bar	0.736
2)	208 bar	0.689
3)	195 bar	0.680
4)	192 bar	0.679
5)	192 bar	

$$\therefore \boxed{P_2 \approx 192 \text{ bar}}$$

with this, we can calculate H_2^R from $P_r = \frac{192}{61.39} = 3.13$

$$\frac{H^R}{RT_c} = \frac{(H^R)^0}{RT_c} + \omega \frac{(H^R)^1}{RT_c}$$

$$= -2.31 + (0.187 \times -0.350)$$

$$= -2.38$$

$$\therefore H^R = -2.38 \times 8.314 \times 308.3 = -6100 \text{ J/mol}$$

from $H^R = U^R + PV^R$, $U^R = H^R - PV^R$

$$U^R = H^R - (Z-1)RT$$

$$= -6100 - (0.679-1) \times 8.314 \times 398$$

$$= -5038 \text{ J/mol}$$

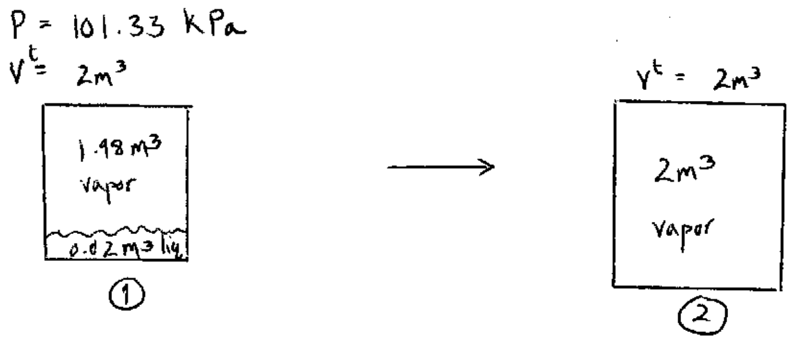
$$\therefore \text{Heat}_{\text{step3}} = -5038 \times 5 = -25190 \text{ J}$$

$$\therefore \text{Total heat} = -635750 + 71914 - 25190$$

$$\boxed{Q = -589026 \text{ J}}$$

Problem 21

a)



For a saturated steam at P = 101.33 KPa, we have

$V^{liq} = 1.044 \ cm^3 g^{-1} \qquad V^{vap} = 1673 \ cm^3 g^{-1}$

$\therefore$ we have $\dfrac{0.02 \times 10^6}{1.044} = 19157 \ g$ of liq water

and $\dfrac{1.98 \times 10^6}{1673} = 1183.5 \ g$ of water vapor

$\therefore \ x = \dfrac{1183.5}{1183.5 + 19157} = 0.0582$

$U_1^t = U^{liq} + x(U^{vap} - U^{liq}) = 419 + 0.058(2506.5 - 419) = 540.5 \ kJ/kg$

At final condition we have $V^t = 2m^3$ and that $x = 1$

$\therefore \ V^{vapor} = \dfrac{2 \times 10^6}{(1183.5 + 19157)} = 98.3 \ cm^3 g^{-1}$

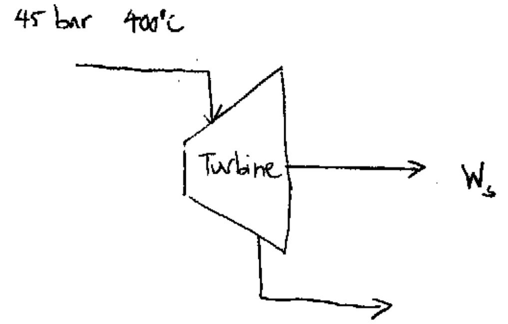
since mass is conserved

for $V^{vap} = 98.3 \ cm^3 g^{-1}$ and $x = 1$ give

$P_2 = 2026 \ KPa \qquad U_2^t = 2598.4 \ kJ/kg$

$$\boxed{\Delta U^t = 2598.4 - 540.5 = 2057.9 \ kJ/kg}$$

b)



From steam table, at inlet conditions of 45 bar, 400°C

$H_1 = 3207.1 \ kJ\,kg^{-1}$ $\quad S_1 = 6.7093 \ kJ\,kg^{-1}K^{-1}$

if the expansion is isentropic then $\Delta S = 0$

ie. $S_2' = S_1 = 6.7093 \ kJ/kg.K$

if we want the steam to be dry, then we want to find the pressure of saturated steam system which has $S^{vap} = S_2$ ie $x' = 1$

it turns out $\Rightarrow$ $P_2 \approx 692 \ kPa$

$H_2' \approx 2761 \ kJ/kg$

$\therefore \ (\Delta H)_s = H_2' - H_1 = -446.1 \ kJ/kg$

$\therefore \ \Delta H = \eta (\Delta H)_s = 0.75 \times -446.1$

$= -335 \ kJ/kg$

$\therefore \ H_2 = H_1 + \Delta H = 3207.1 - 335 = 2872.1 \ kJ/kg$

Note $H_2 > H_2'$ so the steam is still super saturated and as a result, we can expand to and even lower pressure

From steam table search guessing P, with the fact that $S = 6.7093\ kJ/kgK$

we can calculate x from $S = S^{liq} + x(S^{vap} - S^{liq})$.

then calculate $H_2' = H^{liq} + x(H^{vap} - H^{liq})$, which then gives us $(\Delta H)_S$

hence ΔH and H_2, then compare this to $H^{sat\ vap}$

P	H_2	$H^{sat\ vap}$
186.23 kPa	2670 kJ/kg	2703.1 kJ/kg
198.54 kPa	2707 kJ/kg	2706 kJ/kg

$\therefore$ the true P lies between these two pressures. since $H_2 = H^{sat\ vap}$

by interpolation $\boxed{P \approx 196\ kPa}$

which has $H \approx 2700\ kJ/kg$

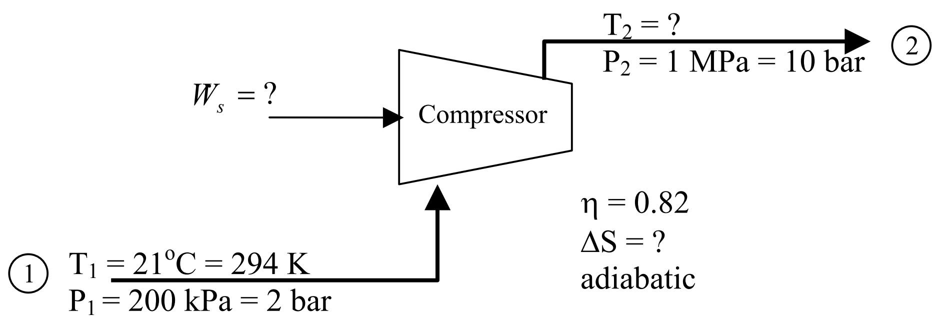
$$\therefore W_s = 2700 - 3207.1$$

$$= -507.1$$

$\therefore$ $\boxed{\text{Work output} = 507.1\ kJ/kg}$

Suppose $\eta = 0.80$, the minimum pressure will be higher than this case

22)



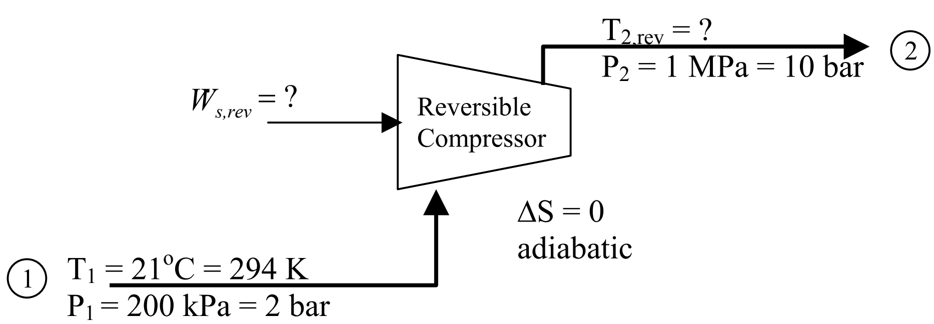
We are given the information above. The unknowns are marked with '?'.

General approach

1) We are given the value of $\eta = \dfrac{(\Delta H)_S}{\Delta H} = \dfrac{\dot{W}_{s,rev}}{\dot{W}_s} = 0.82$. To get $\dot{W}_s$, we need $\dot{W}_{s,rev}$.

$\dot{W}_{s,rev}$ is the shaft work of an adiabatic reversible compressor that goes from T_1 and P_1 to P_2.

2) Imagine a reversible compressor for which $\Delta S = 0$. T_1, P_1, and P_2 are the same as real case. The outlet temperature ($T_{2,rev}$) will be different from the real case (T_2), so will the shaft work.



Compare with the real compressor. $T_{2,rev}$ is so marked to emphasize the difference from real compressor's T_2.

3) We know T_1 and P_1, so state 1 is defined → we can get H_1 and S1.
4) Since $\Delta S = 0$, $S_{2,rev} = S_1$.
5) We know P_2 and $S_{2,rev}$, so state 2 is defined → we can get $T_{2,rev}$ and $H_{2,rev}$.
6) $\dot{W}_{s,rev} = \dot{m}(H_{2,rev} - H_1)$ from 1st law on adiabatic system.

7) $\dot{W}_s = \dot{W}_{s,rev} / \eta$ gives us information about the real case
8) $\dot{W}_s = \dot{m}(H_2 - H_1)$ → we can calculate H_2.
9) We know H_2 and P_2, so state 2 is defined → we can get T_2 and S_2.

We will go through these steps using two methods: generalized correlation and using experimental data.

Note: This part of the problem is very similar to problem 19b in the previous problem set.

a) Generalized correlation

First, looking at the reversible case. We want $\Delta S = 0$. $T_1 = 294$ K, $P_1 = 2$ bar, $P_2 = 10$ bar, $T_{2,rev} = ?$.
(The $_{rev}$ subscript in the $T_{2,rev}$ is just a reminder that it will be different from the real T_2).

$$\Delta S = \Delta S^{ig} + \Delta S^R = 0$$

$$\Delta S = \int_{T_1}^{T_{2,rev}} \frac{Cp^{ig}}{T} dT - \int_{P_1}^{P_2} \frac{R}{P} dP + S_2^R - S_1^R = 0 \qquad (1)$$

From Appendix C, for ammonia, $Cp^{ig} = R(A + BT + CT^2 + DT^{-2})$ (2)
where $A = 3.578$, $B = 3.023 \times 10^{-3}$, $C = 0$, and $D = -0.186 \times 10^5$.

The residuals are to be calculated from generalized correlation.

From appendix B: $T_c = 405.7$, $P_c = 112.8$ bar, and $w = 0.253$ for ammonia.
$P_{r,1} = 2 \text{ bar} / 112.8 \text{ bar} = 0.0177$; $T_{r,1} = 294 \text{ K} / 405.7 \text{ K} = 0.725$
$P_{r,2} = 10 \text{ bar} / 112.8 \text{ bar} = 0.0887$

The reduced pressures are quite low, so we can use equation (6.79) in the book to calculate the residual entropy:

$$\frac{S^R}{R} = -P_r\left(\frac{dB^0}{dT_r} + \omega \frac{dB^1}{dT_r}\right) \quad \text{where} \quad \frac{dB^0}{dT_r} = \frac{0.675}{T_r^{2.6}} \quad \text{and} \quad \frac{dB^1}{dT_r} = \frac{0.722}{T_r^{5.2}} \qquad (3)$$

Note: We *can* use the charts / tables for S^R but since T_2 is not known, it becomes an iterative process: 1) guess T_2, 2) calculate ΔS, 3) if $\Delta S = 0$, done; if not, go to 1). Using these equations is easier in this case.

Putting (1), (2), and (3) together, we get:

$$\Delta S = \underbrace{\int_{T_1}^{T_{2,rev}} R(\frac{A}{T} + B + CT + DT^{-3})\, dT - \int_{P_1}^{P_2} \frac{R}{P} dP}_{\text{ideal gas part}} + \underbrace{\left[-RP_{r2}\left(\frac{0.675}{T_{r2,rev}^{2.6}} + \omega \frac{0.722}{T_{r2,rev}^{5.2}}\right)\right]}_{S^R_2} - \underbrace{\left[-RP_{r1}\left(\frac{0.675}{T_{r1}^{2.6}} + \omega \frac{0.722}{T_{r1}^{5.2}}\right)\right]}_{S^R_1} = 0$$

where $Tr_{2,rev} = T_{2,rev} / T_c$. Expanding the expression:

$$0 = R(A \ln (\frac{T_{2,rev}}{T_1}) + B(T_{2,rev} - T_1) + \frac{C}{2}(T_{2,rev}^2 - T_1^2) - \frac{D}{2}(T_{2,rev}^{-2} - T_1^{-2}) - R \ln (\frac{P_2}{P_1})$$
$$+ \left[-RP_{r2}\left(\frac{0.675}{(T_{2,rev}/T_c)^{2.6}} + \omega \frac{0.722}{(T_{2,rev}/T_c)^{5.2}}\right)\right] - \left[-RP_{r1}\left(\frac{0.675}{T_{r1}^{2.6}} + \omega \frac{0.722}{T_{r1}^{5.2}}\right)\right]$$

Dividing both sides by R removes the R. Writing out known values…

$$0 = (3.578 \ln (\frac{T_{2,rev}}{294}) + 3.020 \cdot 10^{-3}(T_{2,rev} - 294) - \frac{-0.186 \cdot 10^5}{2}(T_{2,rev}^{-2} - T_1^{-2}) - \ln (\frac{10 \text{ bar}}{2 \text{ bar}})$$
$$-0.0887\left(\frac{0.675}{(T_{2,rev}/405.7\text{ K})^{2.6}} + 0.253\frac{0.722}{(T_{2,rev}/405.7\text{ K})^{5.2}}\right) + 0.0177\left(\frac{0.675}{0.725^{2.6}} + 0.253\frac{0.722}{0.725^{5.2}}\right)$$

Thus, the only unknown in the equation above is $T_{2,rev}$.
Solving it with trial-and-error or using your favorite software, you should get $T_{2,rev} = \underline{422.6 \text{ K.}}$

Note: If we use ideal gas law without residual correction, we get $T_{2,rev} = 420.7$. Close because pressure P_r is low.

$$(\Delta H)_S = \qquad \Delta H^{ig} \qquad + \quad \Delta H^R$$

$$(\Delta H)_S = \int_{T_1}^{T_{2,rev}} Cp^{ig} dT \quad + \; H_2^R - H_1^R \qquad (4)$$

Similar to the entropy, we have equation (6.78) to calculate H^R at low pressures:

$$\frac{H^R}{RT_c} = P_r\left[B^0 - T_r\frac{dB^0}{dT_r} + \omega\left(B^1 - T_r\frac{dB^1}{dT_r}\right)\right]$$

$$B^0 = 0.083 - \frac{0.422}{T_r^{1.6}}, \qquad B^1 = 0.139 - \frac{0.172}{T_r^{4.2}}, \qquad \frac{dB^0}{dT_r} = \frac{0.675}{T_r^{2.6}}, \qquad \frac{dB^1}{dT_r} = \frac{0.722}{T_r^{5.2}}$$

Using this and the Cp^{ig} expression in equation 4, we get:

$$(\Delta H)_S = R\left[A(T_{2,rev} - T_1) + \frac{1}{2}B(T_{2,rev}^2 - T_1^2) + \frac{1}{3}C(T_{2,rev}^3 - T_1^3) - D\left(\frac{1}{T_{2,rev}} - \frac{1}{T_1}\right)\right]$$

$$+ P_{r2}\left[0.083 - \frac{0.422}{T_{r,2rev}^{1.6}} - T_{r2,rev}\frac{0.675}{T_{r2,rev}^{2.6}} + \omega\left(0.139 - \frac{0.172}{T_{r2,rev}^{4.2}} - T_{r2,rev}\frac{0.722}{T_{r2,rev}^{5.2}}\right)\right]$$

$$- P_{r1}\left[0.083 - \frac{0.422}{T_{r1}^{1.6}} - T_{r2,rev}\frac{0.675}{T_{r1}^{2.6}} + \omega\left(0.139 - \frac{0.172}{T_{r1}^{4.2}} - T_{r1}\frac{0.722}{T_{r1}^{5.2}}\right)\right]$$

Since we know everything in the equation, we can plug in the numbers to get $(\Delta H)_S$ = <u>4650 J/mol</u>.

1st law: $\dot{W}_{s,rev} = \dot{m}\Delta H$. We are not given the flow rate, so we can only express $\dot{W}_{s,rev}$ in molar basis

$\dot{W}_{s,rev}$ = <u>4650 J/mol</u>

$\dot{W}_s = \dot{W}_{s,rev} / \eta$ = (4650 J/mol) / 0.82 = <u>**5670 J/mol**</u> (ans)

ΔH (real) = ΔH = $\dot{W}_s$ = 5670 J/mol

What about temperature and entropy? We can use the same expression for ΔH : (note $T_2 \neq T_{2,rev}$)

$$\Delta H = 5670\,J/mol = R\left[A(T_2 - T_1) + \frac{1}{2}B(T_2^2 - T_1^2) + \frac{1}{3}C(T_2^3 - T_1^3) - D\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right]$$

$$+ P_{r2}\left[0.083 - \frac{0.422}{T_{r,2}^{1.6}} - T_{r2,rev}\frac{0.675}{T_{r2}^{2.6}} + \omega\left(0.139 - \frac{0.172}{T_{r2}^{4.2}} - T_{r2,rev}\frac{0.722}{T_{r2}^{5.2}}\right)\right]$$

$$- P_{r1}\left[0.083 - \frac{0.422}{T_{r1}^{1.6}} - T_{r2,rev}\frac{0.675}{T_{r1}^{2.6}} + \omega\left(0.139 - \frac{0.172}{T_{r1}^{4.2}} - T_{r1}\frac{0.722}{T_{r1}^{5.2}}\right)\right]$$

We know everything in the equation except for T_2; we can solve for T_2 → T_2 = <u>**447.3 K**</u> (ans)
Finally, since we know T_2, we can use a similar expression for entropy as above:

$$\Delta S = R(A\ln(\frac{T_2}{T_1}) + B(T_2 - T_1) + \frac{C}{2}(T_2^2 - T_1^2) - \frac{D}{2}(T_2^{-2} - T_1^{-2}) - R\ln(\frac{P_2}{P_1}) +$$

$$\left[-RP_{r2}\left(\frac{0.675}{(T_2/T_c)^{2.6}} + \omega\frac{0.722}{(T_2/T_c)^{5.2}}\right)\right] - \left[-RP_{r1}\left(\frac{0.675}{T_{r1}^{2.6}} + \omega\frac{0.722}{T_{r1}^{5.2}}\right)\right]$$

Plugging in all the numbers, we get ΔS = <u>**2.35 J/mol K**</u> (ans) > 0 because irreversible, makes sense.

b) Using experimental data (NIST webbook)

Looking at the reversible case: T_1, P_1 going to $T_{2,rev}$, P_2 with $\Delta S = 0$.

$T_1 = 294$ K, $P_1 = 2$ bar $\rightarrow$ $H_1 = 28.515$ kJ/mol $S_1 = 114.01$ J/mol K

To find the outlet, we search for $T_{2,rev}$ at $P_2 = 10$ bar that gives $S_2 = S_1 = 114.01$ J/mol K (since $\Delta S = 0$)
This is satisfied when $P_2 = 10$ bar and $T_{2,rev}$ = <u>422.1 K.</u> At this condition, $H_2 = 33.149$ kJ/mol

$\dot{W}_{s,rev} = (\Delta H)_S = H_{2,rev} - H_1 = (33.149 - 28.515)$ kJ/mol $= 4634$ J/mol

Note: Again, because we don't know the flow rates, we express work in terms of J/mol

$\dot{W}_s = \dot{W}_{s,rev} / \eta = (4634 \text{ J/mol}) / 0.82 =$ <u>**5651 J/mol**</u> (ans)

$\dot{W}_s / \dot{m} = \Delta H = H_2 - H_1 \rightarrow H_2 = \dot{W}_s + H_1 =$ 5651 J/mol + 28.515 kJ/mol = 34.166 kJ/mol

We now find T_2 at $P_2 = 10$ bar that gives $H_2 = 34.166$ kJ/mol.
This is satisfied when $P_2 = 10$ bar and T_2 = <u>**446.4 K**</u> (ans)

At this condition, $S_2 = 116.36$ J/mol K. Therefore $\Delta S = S_2 - S_1 = (116.36 - 114.01) =$ <u>**2.35 J/mol K**</u> (ans)

Comparing the results from the two methods, we find very good agreement:

	Generalized Correlation	Experimental Data
T_2	447.2 K	446.4 K
$\dot{W}_s$	5670 J/mol	5651 J/mol
ΔS	2.35 J/mol K	2.35 J/mol K

Moral of the story:

a) Experimental data are (by far) easier to use. Use them when you have them!
b) Generalized correlations, though rather unwieldy, are quite accurate.