(P8.1) $G \equiv H - TS$

$$\Rightarrow \frac{G-G^{ig}}{RT} = \frac{H-H^{ig}}{RT} - \frac{S-S^{ig}}{R} \text{ ………………………………………Eqn. 8.21}$$

$$\frac{H-H^{ig}}{RT} = \int_0^\rho -T\left(\frac{\partial Z}{\partial T}\right)_\rho \frac{d\rho}{\rho} + Z - 1 = \int_0^\rho -T\left[\frac{-3}{2}\frac{a\rho}{RT^{5/2}(1+b\rho)}\right]\frac{d\rho}{\rho} + Z - 1$$

note: $\int \frac{dx}{ax+b} = \frac{1}{a}\log_e(ax+b)$

$$= \frac{3}{2T^{3/2}}\left(\frac{1}{b}\ln(1+b\rho)\right)\frac{a}{R}\Bigg|_0^\rho + Z - 1 = \frac{3a}{2RT^{3/2}}\left(\frac{1}{b}\ln(1+b\rho)\right) + Z - 1$$

$$\frac{S-S^{ig}}{R} = \int_0^\rho \left[-T\left(\partial Z\big/\partial T\right)_\rho - (Z-1)\right]\frac{d\rho}{\rho} + \ln Z \text{ ………………………….Eqn. 8.23}$$

$$= \int_0^\rho \left[\frac{3}{2}\frac{a}{RT^{3/2}(1+b\rho)}\right]d\rho - \int_0^\rho \left[\frac{b}{1-b\rho} - \frac{a}{RT^{3/2}(1+b\rho)}\right]\frac{d\rho}{\rho} + \ln Z$$

$$= \frac{3}{2}\frac{a}{RT^{3/2}}\left(\frac{1}{b}\ln(1+b\rho)\right) + \ln(1-b\rho) + \frac{a}{RT^{3/2}}\ln(1+b\rho) + \ln Z$$

$$\Rightarrow \frac{G-G^{ig}}{RT} = \frac{H-H^{ig}}{RT} - \frac{S-S^{ig}}{R}$$

$$\Rightarrow \frac{3a}{2RT^{3/2}}\left(\frac{1}{b}\ln(1+b\rho)\right) + Z - 1 - \left\{\frac{3}{2}\frac{a}{RT^{3/2}}\left(\frac{1}{b}\ln(1+b\rho)\right) + \ln(1-b\rho) + \frac{a}{RT^{3/2}}\ln(1+b\rho) + \ln Z\right\}$$

$$\Rightarrow \frac{G-G^{ig}}{RT} = -\ln(1-b\rho) - \frac{a}{bRT^{3/2}}\ln(1+b\rho) + Z - 1 - \ln Z$$

Or by using Eqn. (8.26)

$$\Rightarrow \frac{G-G^{ig}}{RT} = \int_0^\rho \frac{(Z-1)}{\rho}d\rho + (Z-1) - \ln Z$$

$$\Rightarrow \frac{G-G^{ig}}{RT} = \int_0^\rho \left[\frac{b}{1-b\rho} - \frac{a}{RT^{3/2}(1+b\rho)}\right]\frac{d\rho}{\rho} + (Z-1) - \ln Z$$

$$\Rightarrow \frac{G-G^{ig}}{RT} = -\ln(1-b\rho) - \frac{a}{bRT^{3/2}}\ln(1+b\rho) + Z - 1 - \ln Z$$

(P8.2) $Z = 1 - b\rho / T_r$

Depature function $\Rightarrow \left(\dfrac{H - H^{ig}}{RT}\right) = \int_0^{\rho} -T\left[\dfrac{\partial Z}{\partial T}\right]_{\rho} \dfrac{d\rho}{\rho} + Z - 1$ ………..Eqn. 8.24

$$\Rightarrow \left(\frac{H - H^{ig}}{RT}\right) = \int_0^{\rho} -T_r\left[\frac{b\rho}{T_r^{\,2}}\right]\frac{d\rho}{\rho} - \frac{b\rho}{T_r} = \frac{-T_r b\rho}{T_r^{\,2}} - \frac{b\rho}{T_r} = -\frac{2b\rho}{T_r}$$

(P8.3) (a) $\int_{T_1}^{T_2} Cvdt = \Delta U$, $\Rightarrow \left(\dfrac{\partial U}{\partial T}\right)_V = Cv$

$$\frac{U - U^{ig}}{R} = \int_0^{\rho} -T^2\left(\frac{\partial Z}{\partial T}\right)_{\rho}\frac{d\rho}{\rho}$$

$$\Rightarrow \left(\frac{\partial U}{\partial T}\right)_V = (-2T\left(\frac{dZ}{dT}\right)_{\rho} - T^2\left(\frac{\partial^2 Z}{\partial T^2}\right)_{\rho})\frac{d\rho}{\rho}$$

$$\Rightarrow \frac{Cv - Cv^{ig}}{R} = \int_0^{\rho}(-2T\left(\frac{dZ}{dT}\right)_{\rho} - T^2\left(\frac{\partial^2 Z}{\partial T^2}\right)_{\rho})\frac{d\rho}{\rho}$$

(b) $Z = 1 + \dfrac{b\rho}{1 + b\rho} - \rho\left(\exp(a/T)\right) + \rho$

$$\Rightarrow \left(\frac{dZ}{dT}\right)_{\rho} = \rho\frac{a}{T^2}\left(\exp(a/T)\right)$$

$$\Rightarrow \left(\frac{\partial^2 Z}{\partial T^2}\right)_{\rho} = -2\rho\frac{a}{T^3}\left(\exp(a/T)\right) - \rho\frac{a^2}{T^4}\left(\exp(a/T)\right)$$

$$\Rightarrow \frac{Cv - Cv^{ig}}{R} = \int_0^{\rho}\{-2T\rho\frac{a}{T^2}\left(\exp(a/T)\right) + 2T^2\rho\frac{a}{T^3}\left(\exp(a/T)\right) + \frac{T^2 a^2\rho}{T^4}\left(\exp(a/T)\right)\}\frac{d\rho}{\rho}$$

First two terms cancel, integral with respect to ρ is simple.

$$\Rightarrow \frac{Cv - Cv^{ig}}{R} = \frac{a^2\rho}{T^2}\left(\exp(a/T)\right)$$

(P8.4) Helmholtz Energy, ⇒ A = ??

Departure function, $\Rightarrow \dfrac{A - A^{ig}}{RT} = \dfrac{U - U^{ig}}{RT} - \dfrac{S - S^{ig}}{R}$ …………….Eqn.8.20

$$\frac{U-U^{ig}}{RT}=\int_0^{\rho}-T\left(\frac{\partial Z}{\partial T}\right)_{\rho}\frac{d\rho}{\rho}\text{ ……………………………………………Eqn. 8.22}$$

$$=\int_0^{\rho}-T\left[\frac{9.5N_Ab\varepsilon}{RT^2}\right]d\rho=\frac{-9.5N_Ab\varepsilon}{RT}\rho$$

$$\frac{S-S^{ig}}{R}=\int_0^{\rho}-T\left(\frac{\partial Z}{\partial T}\right)_{\rho}\frac{d\rho}{\rho}-\int_0^{\rho}(Z-1)\frac{d\rho}{\rho}+\ln Z\text{ ………………………Eqn. 8.23}$$

$$=\int_0^{\rho}-T\left[\frac{9.5N_Ab\varepsilon}{RT^2}\right]d\rho-\int_0^{\rho}\left(\frac{4b}{1-b\rho}\right)\frac{d\rho}{\rho}+\int_0^{\rho}\frac{9.5N_Ab\varepsilon}{RT}d\rho+\ln Z$$

$$=\frac{-9.5N_Ab\varepsilon}{RT}\rho+4\ln(1-b\rho)+\frac{9.5N_Ab\varepsilon}{RT}\rho+\ln Z$$

$$\Rightarrow\frac{A-A^{ig}}{RT}=\frac{-9.5N_Ab\varepsilon}{RT}\rho-4\ln(1-b\rho)-\ln Z$$

or by using Eqn. (8.25)

$$\Rightarrow\frac{A-A^{ig}}{RT}=\int_0^{\rho}\left(\frac{Z-1}{\rho}\right)d\rho-\ln Z$$

$$\Rightarrow\frac{A-A^{ig}}{RT}=\int_0^{\rho}\frac{4b}{1-b\rho}d\rho-\int_0^{\rho}\frac{9.5N_Ab\varepsilon}{RT}d\rho-\ln Z$$

$$\Rightarrow\frac{A-A^{ig}}{RT}=\frac{-9.5N_Ab\varepsilon}{RT}\rho-4\ln(1-b\rho)-\ln Z$$

(P8.5) 1g-mole of 1,3 butadiene

$P_1=25bars=2.5MPa$

$P_2=125bars=12.5MPa$

$T_1=400K$

$T_2=550K$

Use PREOS.XLS, use PROPS page

For State 2:						
T (K)	550	Z	V	H-Hig	U-Uig	S-Sig
P (MPa)	12.5		cm3/gmol	J/mol	J/mol	J/molK
& for 1 root region		0.67898224	248.3825681	-8054.423	-6586.505	-11.10052

State 1 has three real roots. Take the more stable root (lower fugacity value).

For State 1							
T (K)	400	Z	V	fugacity	H-Hig	U-Uig	S-Sig

P (MPa)	2.5		cm3/gmol	MPa	J/mol	J/mol	J/molK
answers for three		0.668475	889.2328	1.871218	-3460.25	-2357.73	-6.24206
root region		0.180657	240.3178				
		0.103098	137.145	2.008636	-14993.7	-12011	-35.6649

$$\Delta H = H_2 - H_1 = \left(H_2 - H_2^{ig}\right) + \left(H_2^{ig} - H_1^{ig}\right) - \left(H_1 - H_1^{ig}\right)$$

$$\Delta S = S_2 - S_1 = \left(S_2 - S_2^{ig}\right) + \left(S_2^{ig} - S_1^{ig}\right) - \left(S_1 - S_1^{ig}\right)$$

Find $H_2^{ig} - H_1^{ig} = ??$

$$\Rightarrow H_2^{ig} - H_1^{ig} = \int_{T_1}^{T_2} CpdT = \int_{T_1}^{T_2} (A + BT + CT^2 + DT^3)dT$$

$$= A\left(T_2 - T_1\right) + \frac{B}{2}\left(T_2^2 - T_1^2\right) + \frac{C}{3}\left(T_2^3 - T_1^3\right) + \frac{D}{4}\left(T_2^4 - T_1^4\right)$$

A	B	C	D
-1.687	3.42E-01	-2.34E-04	6.34E-08

$$\Rightarrow H_2^{ig} - H_1^{ig} = 17173.81 J/mole$$

Similarly for $S_2^{ig} - S_1^{ig} = \int_{T_1}^{T_2} \frac{Cp}{T} dT - R\ln\frac{P_2}{P_1}$

$$\Rightarrow S_2^{ig} - S_1^{ig} = \left[A\ln\left(\frac{T_2}{T_1}\right) + B\left(T_2 - T_1\right) + \frac{C}{2}\left(T_2^2 - T_1^2\right) + \frac{D}{3}\left(T_2^3 - T_1^3\right)\right] - R\ln\left(\frac{P_2}{P_1}\right)$$

$$\Rightarrow S_2^{ig} - S_1^{ig} = 22.87 J/mole - K$$

$$\Rightarrow \Delta H = 12579.63 J/mole$$

$$\& \ \Delta S = 18.01 J/mole - K$$

$$\Delta U = \int_{T_1}^{T_2} Cv(T)dT = \Delta H - R\left(T_2 - T_1\right) \quad , \qquad Cv = Cp - R$$

$$U_2^{ig} - U_1^{ig} = 17173.81 - 8.314 * \left(550 - 400\right) = 15926.71 J/mole$$

$$\& \ \Delta U = U_2 - U_1 = \left(U_2 - U_2^{ig}\right) + \left(U_2^{ig} - U_1^{ig}\right) - \left(U_1 - U_1^{ig}\right)$$

$$\Rightarrow \Delta U = 15926.71 - 6586.505 + 2357.73$$

$$\Rightarrow \Delta U = 11697.94 J/mole$$

$$\Delta V = V_2 - V_1 = 248.4 - 889.2$$

$$\Rightarrow \Delta V = -640.8 cm^3/mol$$

(P8.7)

$$T_1 = 623.15K$$

$$P_1 = 5MPa$$

Use PREOS.XLS

$S_1 = S_2'$

T (K)	623.15	Z	V	H	U	S
P (MPa)	5		cm3/gmol	J/mol	J/mol	J/molK
& for 1 root region		0.986361	1022.041	18750.12	13639.92	**9.1954**

$\Rightarrow$ Use Solver in the spread sheet by changing pressure to 0.2MPa and Fixing the entropy value = 9.1954*J/mol-K* and in this case $S_1 = S_2'$=9.1954*J/mole-K* then we can find $\Delta H' and \Delta H$

T (K)	**404.71**	Z	V	H	U	S
P (MPa)	0.2		cm3/gmol	J/mol	J/mol	J/molK
& for 1 root region		0.99499	16739.56	5234.912	1887	**9.1954**

$$\Rightarrow T = 404.71K$$

$$\Delta H' = 5234.912 - 18750.12 = -13515.21 J/mole$$

$$\eta = 0.8 \Rightarrow \frac{\Delta H}{\Delta H'} = 0.8 = \frac{W_s}{W_s'} = \frac{H_2 - H_1}{H_2' - H_1}$$

$$\Rightarrow 0.8 = \frac{H_2 - 18750.12}{5234.912 - 18750.12}$$

$$\Rightarrow H_2 = 7937.95 J/mol$$

$$\Rightarrow \Delta H = H_2 - H_1 = 7937.95 - 18750.12$$

$$\Rightarrow \Delta H = 10812.166 J/mol$$

T (K)	452.012672	fugacity	H	U	S
P (MPa)	0.2	MPa	J/mol	J/mol	J/molK
answers for three root region		#NUM!	#NUM!	#NUM!	#NUM!
		#NUM!	#NUM!	#NUM!	#NUM!
& for 1 root region		0.199324	7937.95	4192.62	15.50748631

$$\Rightarrow T_2 = 452K$$

P8.8 The outlet of the boiler will be 200C, and the outlet of the condenser will be 65 C. Ignore the pressure drops through the boiler and condenser.

Key: Refer to Fig 5.1

4 - outlet of turbine, sat’d vapor at the operating pressure of the condenser (0.1027 MPa)
5 - outlet of condenser, sat’d liquid at 65 C
6 - outlet of pump at the pressure of the boiler (4.087 MPa)
2 - outlet of the boiler at 200 C and 4.087 MPa
3 - outlet of superheater at 4.087 MPa and currently unknown pressure.

Strategy:
The answer requires the net work through the turbine and pump and also requires the heat transfer in the boiler/superheater. For the turbine, we need states 3 and 4, for the pump, we need states 5 and 6, for the boiler/superheater duty, we need states 6 and 3. Therefore of the listed states, we only need 3, 4, 5 and 6. The pump and turbine will be reversible to get maximum efficiency.

Reference state: Choose 298K, 0.1 MPa, take liquid root since it is more stable.

Reference State		For real fluid	Roots						
T (K)	298	reference state	Z	V	fugacity	$H-H^{ig}$	$U-U^{ig}$	$S-S^{ig}$	
P (MPa)	0.1	identifier index		cm^3/gmol	MPa	J/mol	J/mol	J/molK	
0 for H_R = 0, 1 for U_R = 0		1	0.973865	24128.21	0.09745	-181.766	-117.015	-0.39515	answers for three
0			0.02256	558.9447					root region
0 for ig, 1 for real fluid ref		2	0.001922	47.61241	0.015328	-40666.4	-38193.6	-120.856	
1		3	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	& for 1 root region

State 4, saturated vapor at 0.1027 MPa, and 65C

Current State		Roots		Stable Root has a lower fugacity			
T (K)	338.15	Z	V	fugacity	H	U	S
P (MPa)	0.1027		cm^3/gmol	MPa	J/mol	J/mol	J/molK
answers for three		0.9814393	26866.581	0.100826	42337.01	39577.81	126.072
root region		0.0152363	417.0899		33794.35	33751.52	83.07621
		0.0018284	50.051902	0.100788	4618.871	4613.731	14.53248
& for 1 root region		#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!

H_4= 42.337 kJ/mol

State 5, saturated liquid at 65 C from table above, H_5 = 4.619 kJ/mol

State 6, outlet of reversible pump will be at 4.087 MPa and have S = 14.53248 J/mol-K as in State 2. Use solver or goal seek to adjust T at P=4.087MPa to match S=14.53248.

Current State		Roots		Stable Root has a lower fugacity			
T (K)	338.960112	Z	V	fugacity	H	U	S
P (MPa)	4.087		cm^3/gmol	MPa	J/mol	J/mol	J/molK
answers for three		#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!
root region		#NUM!	#NUM!		#NUM!	#NUM!	#NUM!
		#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!
& for 1 root region		0.0724201	49.935951	0.111711	4818.061	4613.972	14.53248

H_6 = 4.818 kJ/mol

State 3, has P=4.087MPa, and the same entropy as State 4, S = 126.072 J/mol-K. Use solver or goal seek to adjust T at this P until S is matched.

Current State		Roots		Stable Root has a lower fugacity			
T (K)	608.605533	Z	V	fugacity	H	U	S
P (MPa)	4.087		cm^3/gmol	MPa	J/mol	J/mol	J/molK
answers for three root region		#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!
		#NUM!	#NUM!		#NUM!	#NUM!	#NUM!
		#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!
& for 1 root region		0.9021541	1116.9198	3.704821	55803.11	51238.26	126.072

H_3 = 55.803 kJ/mol

Therefore, the total work is the sum of the turbine and pump work,
$W_S = (H_4 - H_3) + (H_6 - H_5) = 42.337 - 55.803 + 4.818 - 4.619 = -13.267$ kJ/mol
The heat transfer in the boiler/superheater is:
$Q_H = H_3 - H_6 = 55.803 - 4.818 = 50.985$ kJ/mol
The thermal efficiency is
$\eta = 13.267/50.985 * 100\% = 26\ \%$