(P7.1) $G \equiv H - TS$

$$\Rightarrow \frac{G-G^{ig}}{RT} = \frac{H-H^{ig}}{RT} - \frac{S-S^{ig}}{R} \quad \text{……………………………………Eqn. 7.21}$$

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

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

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

$$\frac{S-S^{ig}}{R} = \int_0^\rho \left[-T\left(\partial Z/\partial T\right)_\rho - (Z-1)\right]\frac{d\rho}{\rho} + \ln Z \quad \text{………………………..Eqn. 7.23}$$

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

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

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

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

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

Or by using Eqn. (7.26)

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

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

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

(P7.2) $Z = 1 - b\rho / T_r$

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. 7.24

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

(P7.3) (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.

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

(P7.4) Helmholtz Energy, $\Rightarrow$ A = ??

Depature function, $\Rightarrow \dfrac{A-A^{ig}}{RT} = \dfrac{U-U^{ig}}{RT} - \dfrac{S-S^{ig}}{R}$ ……………Eqn.7.20

$$\frac{U-U^{ig}}{RT} = \int_0^\rho -T\left(\frac{\partial Z}{\partial T}\right)_\rho \frac{d\rho}{\rho} \quad \text{……………………………………………Eqn. 7.22}$$

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

$$\frac{S-S^{ig}}{R} = \int_0^\rho -T\left(\frac{\partial Z}{\partial T}\right)_\rho \frac{d\rho}{\rho} - \int_0^\rho (Z-1)\frac{d\rho}{\rho} + \ln Z \quad \text{………………………Eqn. 7.23}$$

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

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

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

or by using Eqn. (7.25)

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

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

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

(P7.5) Compute ΔH,ΔS,ΔU,ΔV of 1,3 butadiene from 25bar,400K to 125bar,550K.

For State 2:

		Z	V	H-Hig	U-Uig	S-Sig
T (K)	550					
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

		Z	V	fugacity	H-Hig	U-Uig	S-Sig
T (K)	400						
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 $H_2^{ig} - H_1^{ig} = ??$

$$\Rightarrow H_2^{ig} - H_1^{ig} = \int_{T_1}^{T_2} Cp dT = \int_{T_1}^{T_2} (A + BT + CT^2 + DT^3) dT$$
$$= A(T_2 - T_1) + \frac{B}{2}\left(T_2^2 - T_1^2\right) + \frac{C}{3}\left(T_2^3 - T_1^3\right) + \frac{D}{4}\left(T_2^4 - T_1^4\right)$$

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

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

$$\Rightarrow S_2^{ig} - S_1^{ig} = 22.87 J/mole - K$$
$$\Rightarrow \Delta H = 12579.63 J/mole$$
$$\& \ \Delta S = 18.01 J/mole - K$$

$$\Delta U = \int_{T_1}^{T_2} Cv(T) dT = \Delta H - R(T_2 - T_1) \quad , \qquad Cv = Cp - R$$
$$U_2^{ig} - U_1^{ig} = 17173.81 - 8.314 * (550 - 400) = 15926.71 J/mole$$
$$\& \ \Delta U = U_2 - U_1 = \left(U_2 - U_2^{ig}\right) + \left(U_2^{ig} - U_1^{ig}\right) - \left(U_1 - U_1^{ig}\right)$$
$$\Rightarrow \Delta U = 15926.71 - 6586.505 + 2357.73$$
$$\Rightarrow \Delta U = 11697.94 J/mole$$

$$\Delta V = V_2 - V_1 = 248.4 - 889.2$$
$$\Rightarrow \Delta V = -640.8 cm^3/mol$$

(P7.6) Ethane tank leaks to turbine: $T = 425K, P_1 = 10MPa, V_1 = 1m^3 \Rightarrow n = 2830 moles$;
Solution: Ebal: ΔH=W; Sbal: ΔS=0.
(a) Compute ToutInitial. Sout=Sin=78.2J/Mol-K<79.7=SsatVap(1bar)⇒ Tout=184.2K
(b) Compute Winitial = ΔH; q=78.2/79.7=98% ⇒ Hout=0.98*14676=14383
W = 14382-24087= -9705J/mol (FYI: given answer at 8880 probably used SRK.)

(P7.7) Compute W for 80% eff turbine on Ethylene from 350°C,50bar to 2bar. Compare Tf for this process to Tf of 100%eff turbine

Solution: Ebal: ΔH=W; Sbal: $S_2' = S_1$=9.1954; Ref=298.15K,1bar, id gas.

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**

For Rev: Use Solver at 0.2MPa and S2'=9.1954*J/mol-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**

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

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

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

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

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

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

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

$$\Rightarrow T_2 = 452K$$

(P7.8) Rankine on methanol, see figure 4.3 page 143. Ref=336.7,0.1Liq.

State	T(K)	P(Mpa)	H	S
4'sat vap	337.4	0.1027	37853	112.16
5 sat liq	337.4	0.1027	73	0.23
3	610	4.087	51458	112.16

$$\eta = \frac{-W}{Q_H} = \frac{(51458 - 37853)}{(51458 - 73)} = 0.2647$$ **(Note: neglecting pump work.)**

(P7.9) Use the energy equation to get (*U-Uig*)/*RT*.

a. For SW fluid for g=10-5x. x=r/σ;

$$\frac{U - U_{ig}}{RT} = \frac{N_A\rho}{2}\int_0^\infty \frac{N_A u}{RT} g(r) 4\pi r^2 dr = \frac{-\varepsilon N_A \rho\sigma^3}{2k_B T}\int_1^{1.5}(10-5x)4\pi x^2 dx = \frac{-\varepsilon N_A 4\pi\rho\sigma^3}{2k_B T}\left[\frac{10x^3}{3} - \frac{5x^4}{4}\right]_1^{1.5}$$

$N_A\rho\sigma^3 = 1$; $\varepsilon/k_BT = 1 \Rightarrow (U\text{-}Uig)/RT = -5.7\pi$.

b. For Sutherland potential with $g = 1+2/x^2$.

$$\frac{U - U_{ig}}{RT} = \frac{N_A\rho}{2}\int_0^\infty \frac{N_A u}{RT} g(r) 4\pi r^2 dr = \frac{-\varepsilon N_A \rho\sigma^3}{2k_B T}\int_1^\infty \left(1 + \frac{2}{x^2}\right)\frac{4\pi x^2}{x^6} dx = \frac{-\varepsilon N_A 4\pi\rho\sigma^3}{2k_B T}\left[\frac{-x^{-3}}{4} - \frac{2x^{-5}}{5}\right]_1^\infty \quad N_A\rho\sigma^3$$

$= 1$; $\varepsilon/k_BT = 1 \Rightarrow (U\text{-}Uig)/RT = -3\pi$.