Introductory Chemical Engineering Thermodynamics

CHAPTER 8

(8.01)What form does the derivative $(\partial Cv/\partial V)_T$ have for vdW and RK EOSs?

$(U\text{-}Uig)/RT = \int -T(\partial Z/\partial T)\rho\ (d\rho/\rho)$; $U = (U\text{-}Uig) + Uig$

$Cv \equiv (\partial U/\partial T)_V = (\partial(U\text{-}Uig)/\partial T)_V + Cvig$

For vdW, $(\partial U/\partial T)_V = -a\rho \Rightarrow (\partial(U\text{-}Uig)/\partial V)_T = 0$ And $(\partial Cv/\partial V)_T = 0$.

For RK, $(U\text{-}Uig)(\partial U/\partial T)_V = -a\rho\ /[T^{1/2}(1+b\rho)] \Rightarrow (\partial(U\text{-}Uig)/\partial T)_V = +\ {}^{1}\!/_{2}\ a\rho\ /[T^{1.5}(1+b\rho)]$

And $(\partial Cv/\partial V)_T = -\rho^2\ (\partial Cv/\partial \rho)_T = -{}^{1}\!/_{2}(a\rho^2/T^{1.5})*[1/(1+b\rho)-b\rho/(1+b\rho)^2] \neq 0$.

Comment:

The RK equation is probably more accurate than the vdW, but not as accurate as PR or SRK. Lee-Kesler gives the most accurate enthalpies. On the other hand, the PR and SRK are more easily adapted for accurate VLE.

Alt:

a) $$\left(\frac{\partial C_V}{\partial V}\right)_T = \frac{\partial}{\partial V}\left[\left(\frac{\partial U}{\partial T}\right)_V\right]_T = \frac{\partial}{\partial T}\left[\left(\frac{\partial U}{\partial V}\right)_T\right]_V \left(\frac{\partial C_V}{\partial V}\right)_T = \frac{\partial}{\partial V}\left[\left(\frac{\partial U}{\partial T}\right)_V\right]_T = \frac{\partial}{\partial T}\left[\left(\frac{\partial U}{\partial V}\right)_T\right]_V$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \quad \Rightarrow \text{ Hence, } \left(\frac{\partial C_V}{\partial V}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V \left(\frac{\partial C_V}{\partial V}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V$$

b) For an ideal gas, $PV = RT\ PV = RT$

$$\left(\frac{\partial^2 P}{\partial T^2}\right)_V = 0, \quad \therefore \left(\frac{\partial C_V}{\partial V}\right)_T = 0$$

c) For a VDW gas, $P = RT/(V\text{-}b) - a\rho$

$$\left(\frac{\partial^2 P}{\partial T^2}\right)_V = 0, \quad \therefore \left(\frac{\partial C_V}{\partial V}\right)_T = 0$$

For a R-K gas, $P = RT/(V\text{-}b) - a/[T^{1/2} * V(V+b)]$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b} - \frac{a}{V(V+b)}\left(-\frac{1}{2}T^{-3/2}\right); \quad \left(\frac{\partial^2 P}{\partial T^2}\right)_V = -\frac{3}{4}\frac{a}{T^{5/2}V(V+b)}$$

$$\therefore \left(\frac{\partial C_V}{\partial V}\right)_T = -\frac{3}{4}\frac{a}{T^{3/2}V(V+b)} \neq 0$$

(8.02) Estimate C_P, C_V and the difference C_P-C_V in (J/mol-K) …(given data below)

T(°F)	P(psia)	V(ft^3/lb)	H (BTU/lb)	U(BTU/lb)
20	14.7	0.02661	-780.22	-780.2924302
40	1400	0.02662	-765.05	-771.9507097
0	14.7	0.02618	-791.24	-791.3112598

n-butane

T(°F)	P(psia)	V(ft3/lb)	(BTU/lb)	U(BTU/lb)
20	14.7	0.02661	-780.22	-780.2924302
40	1400	0.02662	-765.05	-771.9507097
0	14.7	0.02618	-791.24	-791.3112598

Cp(BTU/lb-R)	0.551	Cp/R	16.08354
Cv(BTU/lb-R)	0.417086026	Cv/R	12.17463
		Cp-Cv	32.4987 J/mol-K

Solution:

(8.03) Estimate C_P, C_V and the difference C_P-C_V in (J/mol-K) … (Peng-Robinson)…

C_P^{ig} is calculated from the polynomial in the appendix. $Cv^{ig} = C_P^{ig} - R$

from Ex. 7.6,

$$C_V - C_V^{ig} = \int_{\infty}^{V}\left(\frac{\partial C_V}{\partial V}\right)_T dV = \left(\frac{d^2a}{dT^2}\right)\int_0^{\rho}\frac{T\rho^2}{1+2b\rho-b^2\rho^2}\frac{d\rho}{\rho^2} = \frac{T}{2\sqrt{2}b}\left(\frac{d^2a}{dT^2}\right)\ln\left[\frac{1+\left(1+\sqrt{2}\right)b\rho}{1+\left(1-\sqrt{2}\right)b\rho}\right]$$

$$\frac{d^2a}{dT^2} = \frac{\alpha_c\kappa}{2T_c^2T_r}\left[\kappa+\sqrt{\frac{\alpha}{T_r}}\right]$$

These can be programmed into PREOS.xls to calculate Cv.

To find Cp, starting with Ex. 6.12, we may write

$$C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_P = {-T\left(\frac{\partial P}{\partial T}\right)_V^2}\Big/{\left(\frac{\partial P}{\partial V}\right)_T}$$

By writing in this way, implicit differentiation is avoided. For the PR EOS,

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b} - \frac{1}{V^2+2bV-b^2}\frac{da}{dT}$$

$$\left(\frac{\partial P}{\partial V}\right)_T = \frac{-RT}{(V-b)^2} + \frac{2a(V+b)}{\left(V^2+2bV-b^2\right)^2}$$

The results are:

Gas	T_c (K)	P_c (MPa)	ω	R(cm^{3}MPa/molK)
Butane	425.2	3.797	0.193	8.314

Current State		Roots							
T (K)	298	Z	V	fugacity	rho	Cv-Cvig	(dP/dV)T	(dP/dT)V	Cp-Cv
P (MPa)	0.245		cm^3/gmol	MPa	gmol/cm3				
answers for three		0.92967	9401.31	0.22881	0.00011	0.24563	-2.412E-05	0.0009258	10.5874
		0.00956	96.6505	0.22913	0.01035	15.9536	-2.31747	0.5147196	34.0677

d2a/dT2	7.808544
da/dT	-3101.683

(8.04) Derive the integrals necessary for departure functions…

$(U-U^{ig})/RT = (H - H^{ig})/RT - Z + 1 = -\int_0^P T\left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} - Z + 1$

$(G-G^{ig})/RT = (H-H^{ig})/RT - (S-S^{ig})/R = \int_0^P \frac{(Z-1)}{P} dP$

$(A-A^{ig})/RT = (G-G^{ig})/RT - Z+1 = \int_0^P \frac{(Z-1)}{P} dP - Z + 1$

(8.05) (a) Derive the enthalpy and entropy departure…

a) $$\frac{H-H^{ig}}{RT} = \int_0^\rho -T\left(\frac{\partial Z}{\partial T}\right)_\rho \frac{\partial\rho}{\rho} + Z - 1 \; \frac{H-H^{ig}}{RT} = \int_0^\rho -T\left(\frac{\partial Z}{\partial T}\right)_\rho \frac{\partial\rho}{\rho} + Z - 1$$

$$\frac{S-S^{ig}}{R} = \int_0^\rho \left[-T\left(\frac{\partial Z}{\partial T}\right)_\rho - (Z-1)\right]\frac{\partial\rho}{\rho} + \ln Z$$

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

$$\frac{PV}{RT} = \frac{V}{V-b} - \frac{a}{VRT} \qquad Z = \frac{1}{1-b\rho} - \frac{a\rho}{RT}$$

$$Z - 1 = \frac{b\rho}{1-b\rho} - \frac{a\rho}{RT}$$

$$\left(\frac{\partial Z}{\partial T}\right)_\rho = \frac{a\rho}{RT^2}$$

$$\frac{H-H^{ig}}{RT} = \int_0^\rho -\frac{a\rho}{RT}\frac{\partial\rho}{\rho} + Z - 1$$

$$= -\frac{a\rho}{RT} + Z - 1 = \frac{b\rho}{1-b\rho} - \frac{2a\rho}{RT} = \frac{B}{B-Z} - 2\frac{A}{Z}$$

$$\frac{S-S^{ig}}{R} = \int_0^\rho -\frac{b\rho}{1-b\rho}\frac{\partial\rho}{\rho} + \ln Z$$

$$= \ln(1-b\rho) + \ln Z$$

Note: $\ln(1-b\rho) + \ln Z = \ln(1-B/Z) + \ln Z = \ln(Z-B)$

b) Since $G = H - TS$

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

$$= \frac{b\rho}{1-b\rho} - \frac{2a\rho}{RT} - \ln(1-b\rho) - \ln Z$$

Note: $\ln\left(\frac{f}{P}\right) = \frac{b\rho}{1-b\rho} - \frac{2a\rho}{RT} - \ln(1-b\rho) - \ln Z = \frac{B}{B-Z} - 2\frac{A}{Z} - \ln\left(\frac{Z-B}{Z}\right) - \ln Z$

$\ln\frac{f}{P} = \frac{B}{B-Z} - 2\frac{A}{Z} - \ln(Z-B)$

(8.06) Derive expression for enthalpy departure function in terms of the Soave…

Solution:

$$Z = \frac{1}{1-b\rho} - \frac{a}{bRT} \times \frac{b\rho}{1+b\rho}$$

$$a = a_c \alpha$$

$$b = 0.08664 \frac{RT_c}{P_c}$$

$$\alpha = \left[1+\kappa(1-\sqrt{T_r})\right]^2$$

$$\kappa = 0.480 + 1.574\omega - 0.17\omega^2$$

$$\frac{H-H^{ig}}{RT} = \int_0^{\rho} -T\left(\frac{dZ}{dT}\right)\frac{d\rho}{\rho} + Z - 1$$

$$\left(\frac{\partial Z}{\partial T}\right)_\rho = \frac{\partial}{\partial T}\left[\frac{1}{1-b\rho} - \frac{a}{bRT} \times \frac{b\rho}{1+b\rho}\right]_\rho$$

$$\left(\frac{\partial Z}{\partial T}\right)_\rho = -\frac{b\rho}{1+b\rho} * \frac{1}{bR}\frac{\partial}{\partial T}\left[\frac{a_c \alpha}{T}\right] = -\frac{b\rho}{1+b\rho} * \frac{a_c}{bR}\frac{\partial}{\partial T}\left(\frac{\left[1+\kappa(1-\sqrt{T_r})\right]^2}{T}\right)$$

$$\frac{\partial\left(\frac{\alpha}{T}\right)}{\partial T} = F(T); \quad \therefore \left(\frac{\partial Z}{\partial T}\right)_\rho = -\frac{b\rho}{1+b\rho} * \frac{a_c}{bR} * F(T)$$

$$\frac{H-H^{ig}}{RT} = \int_0^{\rho} \frac{Ta_c F(T)}{bR}\frac{db\rho}{1+b\rho} + Z - 1 = \frac{Ta_c F(T)}{bR}\ln(1+b\rho) + Z - 1$$

$d\alpha/dT$ has the same form as PREOS and that can be used.

$$F(T) = d(\alpha/T)/dT = (1/T)(d\alpha/dT) - \alpha/T^2$$

$$= (1/T^2)[-\kappa\sqrt{\alpha T_r} - \alpha]$$

$$\frac{H-H^{ig}}{RT} = \frac{-a_c[\kappa\sqrt{\alpha T_r} + \alpha]}{bRT}\ln(1+b\rho) + Z - 1 = -\frac{A}{B}(1+\kappa\sqrt{T_r/\alpha})\ln((Z+B)/Z) + Z - 1$$

$$\frac{G-Gig}{RT} = \int_0^{b\rho} (Z-1)\frac{dx}{x} + Z - 1 = -\ln(1-b\rho) - \frac{a}{bRT}\ln(1+b\rho) + Z - 1 - \ln Z$$

$$= -\ln(Z-B) - \frac{A}{B}\ln\left(\frac{Z+B}{Z}\right) + Z - 1$$

$$\frac{S-S^{ig}}{R} = \frac{H-H^{ig}}{RT} - \frac{G-G^{ig}}{RT} = Z - 1 + \left[\frac{-a}{bRT} - \frac{a_c\kappa\sqrt{\alpha T_r}}{bRT}\right]\ln(1+b\rho)$$

$$-\left[-\ln(1-b\rho) - \frac{a}{bRT}\ln(1+b\rho) + Z - 1 - \ln Z\right]$$

$$\frac{S-S^{ig}}{R} = \frac{H-H^{ig}}{RT} - \frac{G-G^{ig}}{RT} = +\ln(1-b\rho) - \frac{a_c\kappa\sqrt{\alpha T_r}}{bRT}\ln(1+b\rho) + \ln Z =$$

$$\ln(Z-B) - \frac{A\kappa\sqrt{T_r/\alpha}}{B}\ln\left(\frac{Z+B}{Z}\right)$$

(8.07) In example 8.2, we wrote the equation of state in terms of Z…

$$\frac{PV}{RT}=1+\frac{aP}{RT} \qquad (Z-1)=\frac{aP}{RT} \qquad \left(\frac{\partial Z}{\partial T}\right)_p=-\frac{aP}{RT^2}$$

$$\frac{S-S^{ig}}{R}=-\int_0^P\left[(Z-1)+T\left(\frac{\partial Z}{\partial T}\right)_P\right]\frac{\partial P}{P}=0$$

Rest of the problem is the same!

$$\frac{H-H^{ig}}{RT}=\int_0^P-T\left(\frac{\partial Z}{\partial T}\right)_P\frac{\partial P}{P}$$

$$=\int_0^P\frac{aP}{RT}\frac{\partial P}{P}=\frac{aP}{RT}$$

(8.08) Derive the enthalpy departure function for the ESD equation of state.

$$Z=1+\frac{4c\eta}{1-1.9\eta}-\frac{9.5qY\eta}{1+1.7745Y\eta}$$

$$Note:\frac{H-H^{ig}}{RT}=\frac{U-U^{ig}}{RT}+Z-1=\beta\frac{\partial\left(\left(A-A^{ig}\right)/RT\right)}{\partial\beta}+Z-1$$

$$\frac{A-A^{ig}}{RT}=\int_0^\rho\frac{Z-1}{\rho}d\rho=\int_0^\eta\frac{4c\eta}{1-1.9\eta}\frac{d\eta}{\eta}-\int_0^\eta\frac{9.5qY\eta}{1+1.7745Y\eta}\frac{d\eta}{\eta}$$

$$\frac{A-A^{ig}}{RT}=\frac{-4c}{1.9}\ln(1-1.9\eta)-\frac{9.5q}{1.7745}\ln(1+1.7745Y\eta)$$

$$\beta\frac{\partial\left(\left(A-A^{ig}\right)/RT\right)}{\partial\beta}=0-\frac{9.5q\eta}{1+1.7745Y\eta}\beta\frac{\partial Y}{\partial\beta}$$

$$\beta\frac{\partial Y}{\partial\beta}=\beta\varepsilon\exp(\beta\varepsilon)=\beta\varepsilon(Y+1.0617)$$

$$\frac{H-H^{ig}}{RT}=\frac{9.5q\eta\beta\varepsilon(Y+1.0617)}{1+1.7745Y\eta}+Z-1$$

(8.09-) A gas has a constant-pressure ideal-gas heat capacity of 15R…

$$\left(\frac{\partial Z}{\partial T}\right)_P=-\frac{aP}{RT^2}$$

a. $$\frac{(H-H^{ig})}{RT}=\int_0^P T\left(\frac{aP}{RT^2}\right)\frac{dP}{P}=\frac{aP}{RT}$$

b. State 1, $(H-H^{ig})/RT$ = -1000(0.1)/8.314/300 = -4.01 E-2, $(H-H^{ig})_1$ = -100 J/mol
State 2, $(H-H^{ig})/RT$ = -1000(10)/8.314/400 = -3.07, $(H-H^{ig})_2$ = -10000 J/mol
$(H_2 - H_1)^{ig}$ = 124.71(100) = 12471 J/mol
$H_2 - H_1$ = -10000 + 12471 + 100 = 2571 J/mol

(8.10) Derive the integrated formula for the Helmholtz energy departure ...

Solution:

$A = U - TS = H - PV - TS$

$$\frac{(A-A^{ig})}{RT} = \frac{(H-H^{ig})}{RT} - \frac{(S-S^{ig})}{R} - Z + 1$$

Using the form for $Z = Z(T,P)$: $\int_0^P \frac{(Z-1)}{P}dP - Z + 1 = \frac{BP}{RT} - \frac{BP}{RT} = 0$

(8.11) Recent research suggests the following, known as the PC-SAFT model.

$$\frac{(A-Aig)_{TV}}{RT} = \frac{m\eta(4-3\eta)}{(1-\eta)^2} - (m-1)\ln\left(\frac{5-2\eta}{(1-\eta)^3}\right) - A1\beta\varepsilon - A2(\beta\varepsilon)$$

$$A1 = 12m\eta\sum_0^6 a_i\eta^i \; ; \; A2 = {m^2 6\eta^2 \sum_0^6 b_i\eta^i} \Bigg/ {1 + \frac{4m\eta(2-\eta/2)}{(1-\eta)^4} + (1-m)\frac{4\eta(20-27\eta+12\eta^2-2\eta^3}{[(1-\eta)(2-\eta)]^2}}$$

(a) Derive an expression for Z.

(b) Derive the departure function for $(U\text{-}Uig)/RT$.

Solution: (a) $Z - 1 = \eta(\partial[(A\text{-}Aig)/RT]/\partial\eta)_T \equiv Z0 - Z1\beta\varepsilon - Z2\,(\beta\varepsilon)^2$.

$$Z0 = \frac{m(4-6\eta)}{(1-\eta)^2} + \frac{2m\eta(4-3\eta)}{(1-\eta)^3} - (m-1)\left(\frac{-2}{5-2\eta} - \frac{-3}{(1-\eta)^3}\right); \; Z1 = 12m\eta\sum_0^6 a_i(i+1)\eta^i$$

$$Let\, D \equiv 1 + \frac{4m\eta(2-\eta/2)}{(1-\eta)^4} + (1-m)\frac{4\eta(20-27\eta+12\eta^2-2\eta^3}{[(1-\eta)(2-\eta)]^2}$$

$$Z2 = {}^{1}\!/_{D}\left(m^2 6\eta^2\sum_0^6 b_i(i+2)\eta^i\right) - {}^{1}\!/_{D^2}\left(m^2 6\eta^2\sum_0^6 b_i\eta^i\right)\left(\frac{\eta\partial D}{\partial\eta}\right)$$

$$\frac{\eta\partial D}{\partial\eta} = \frac{4m(2-\eta)}{(1-\eta)^4} + \frac{16m\eta(2-\eta/2)}{(1-\eta)^5} + (1-m)\left(\frac{4(20-54\eta+36\eta^2-8\eta^3}{[(1-\eta)(2-\eta)]^2} + \frac{8\eta(20-27\eta+12\eta^2-2\eta^3}{[(1-\eta)(2-\eta)]^3}(3-2\eta)\right)$$

(b) $(U\text{-}Uig)/RT = \beta(\partial[(A\text{-}Aig)/RT]/\partial\beta)_\eta \equiv -\,A1\beta\varepsilon - 2A2\,(\beta\varepsilon)^2$.

(8.12) Recent research suggests the following EOS… Derive (A-Aig) and (U-Uig)…

$$Z - 1 = \frac{4\eta}{(1-1.9\eta)} - \frac{9.5\eta}{T + 0.7\exp(-10\eta)}$$

$$u = 0.7 + T\exp(10\eta); du/d\eta = 10T\exp(10\eta)$$

$$\Rightarrow\text{"}guess\text{"}\frac{(A-Aig)_{TV}}{RT} = -\frac{4}{1.9}\ln(1-1.9\eta) - \frac{9.5}{10T}\ln(0.7 + T\exp(10\eta))$$

$$\Rightarrow\text{"}check\text{"}\, Z - 1 = -\frac{4\eta}{(1-1.9\eta)} - \frac{9.5\eta\exp(10\eta)}{0.7 + T\exp(10\eta)} = \frac{4\eta}{(1-1.9\eta)} - \frac{9.5\eta}{0.7\exp(-10\eta) + T}$$

(b) (U-Uig)/RT = $-T(\partial[(A\text{-}Aig)/RT]/\partial T)_\eta = \dfrac{9.5\eta}{\left(0.7\exp(-10\eta) + T\right)^2}$

(8.13) A gas is to be compressed in a steady-state flow reversible isothermal…

$$Z = 1 - \frac{aP}{RT^2} + \frac{bP}{RT};$$

$$\frac{H-H^{ig}}{RT}=-T\int_0^P\left(\frac{\partial Z}{\partial T}\right)_P\frac{dP}{P};\ \left(\frac{\partial Z}{\partial T}\right)_P=\frac{2aP}{RT^3}-\frac{bP}{RT^2};\ \frac{H-H^{ig}}{RT}=\frac{-2aP}{RT^2}+\frac{bP}{RT}$$

$$\frac{S-S^{ig}}{R}=-\int_0^P\left[\frac{-aP}{RT^2}+\frac{bP}{RT}\right]\frac{dP}{P}-\frac{2aP}{RT^2}+\frac{bP}{RT}=-\frac{aP}{RT^2}$$

E-bal $\Delta H = Q + W_S$

S-bal $T\Delta S = Q$

$$\Delta H=\left(b-\frac{2a}{T}\right)(P_2-P_1)=\left[15.23-\frac{2(385.2)}{300}\right](20-1)=241\text{ J/mol}$$

$$\Delta S=-\frac{a}{T^2}(P_2-P_1)-R\ln\frac{P_2}{P_1}=-24.99\text{ J/mol-K; Q = -7496 J/mol}$$

Plugging Q into E-balance, $W_S = 7737$ J/mol

Note: H and S departures may also be solved with more complexity using the density integral.

By Eqn. 8.24 $\left(\frac{H-H^{ig}}{RT}\right)=\int_0^\rho -T\left(\frac{\partial Z}{\partial T}\right)_\rho\frac{d\rho}{\rho}+Z-1$

$$\therefore Z=\frac{P}{\rho RT}=\frac{PV}{RT}=1-\frac{aP}{RT^2}+\frac{bP}{RT}=1-\frac{aZ\rho}{T}+bZ\rho=\frac{T}{T+a\rho-b\rho T}$$

Based on $\frac{d}{dx}\left[\frac{f(x)}{g(x)}\right]=\frac{g(x)f'(x)-f(x)g'(x)}{\left[g(x)^2\right]}$

$$\left(\frac{\partial Z}{\partial T}\right)_\rho=\frac{(T+a\rho-b\rho T)-T\bullet(1-b\rho)}{(T+a\rho-b\rho T)^2}=\frac{a\rho}{(T+a\rho-b\rho T)^2}$$

$$\int_0^\rho -T\left(\frac{\partial Z}{\partial T}\right)_\rho\frac{d\rho}{\rho}=-\int_0^\rho\frac{aT}{\left[(a-bT)\rho+T\right]^2}d\rho\ \text{ substitution: }\ \begin{aligned}u&=T+(a-bT)\rho\\ du&=(a-bT)d\rho\end{aligned}$$

$$-\int_T^{T+(a-bT)\rho}\frac{aT}{(a-bT)u^2}du=\frac{a}{(a-bT)}\frac{T}{u}\bigg|_T^{T+(a-bT)\rho}=\frac{a}{(a-bT)}\left(-1+\frac{T}{T+(a-bT)\rho}\right)$$

$$=\frac{a}{a-bT}(Z-1)=\frac{a}{a-bT}\left(b-\frac{a}{T}\right)\frac{P}{RT}=-\frac{aP}{RT^2}$$

$$\therefore\left(\frac{H-H^{ig}}{RT}\right)=\int_0^\rho -T\left(\frac{\partial Z}{\partial T}\right)_\rho\frac{d\rho}{\rho}+Z-1=Z-1-\frac{aP}{RT^2}=\frac{bP}{RT}-\frac{2aP}{RT^2}$$

(8.14) An 1-m^3 isolated chamber with rigid walls is divided into two…

a) Energy balance

$\Delta U = 0$

Entropy balance

$\Delta \underline{S} = \Delta \underline{S}_{gen}$

b) Need departure function for U. First get departure for H and use H = U + PV

$$\frac{H-H^{ig}}{RT}-Z+1=\frac{U-U^{ig}}{RT}$$

$$Z=1+\frac{bP}{RT}-\frac{aP}{RT^2}$$

$$-T\left(\frac{\partial Z}{\partial T}\right)_P=\frac{bT}{RT^2}-\frac{2aPT}{RT^3}$$

$$\frac{H-H^{ig}}{RT}=\int_0^P\left(\frac{bP}{RT}-\frac{2aP}{RT^2}\right)\frac{dP}{P}=\frac{bP}{RT}-\frac{2aP}{RT^2}$$

$$1-Z=-\left(b-\frac{a}{T}\right)\frac{P}{RT}$$

$$U-U^{ig}=\frac{RT}{RT}\left[\left(bP-\frac{2aP}{T}\right)-bP+\frac{aP}{T}\right]$$

$$U-U^{ig}=-\frac{aP}{T}$$

c) Set $U^{ig}{}_R = 0$, set $T_R = 300$ K and $P_R = 2$ MPa

$U^i=\left(U-U^{ig}\right)^i+\int_{T_R}^{T^i}\left(C_P-R\right)dT$ = -40000(5)/300 = -667 J/mol

$U^f=\left(U-U^{ig}\right)^f+\int_{T_R}^{T^f}\left(C_P-R\right)dT=U^i$ = -40000(P)/(T) + 33.53 (T -300) + 0.042 (T^2 - 300^2) = -667 J/mol

Z^i = 0.773, V^i = ZRT/P = 0.773(8.314)(300)/5 = 385.5cm^3/mol

$V^f=\frac{RT}{P}+\left(b-\frac{a}{T}\right)=2V^i$ = 771 cm^3/mol

Programming in Excel and solving,
Solve two equations and two unknowns.
obj 1= -40000(P)/(T) + 33.53 (T -300) + 0.042 (T^2 - 300^2) +667
obj 2 = 8.314T/P + b-a/T -771

Solver gives T = 295 K, P = 2.76 MPa

	final	initial
P	2.766503	5
T	295.0177	300
V	771.0133	385.5067
Z	0.869631	0.772806
U		-666.6667
obj 1	-2.36E-09	
obj 2	-2.25E-07	

(8.15) P-V-T behavior of a simple fluid is found to obey the equation of state

a) $Z=1+\left(b-\frac{a}{T}\right)\frac{P}{RT}$

form $Z = f(T,P)$

$$\frac{H-H^{ig}}{RT} = -\int_0^P T\left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P}$$

$$\left(\frac{\partial Z}{\partial T}\right)_P = -\frac{bP}{RT^2} + \frac{2aP}{RT^3}$$

$$-\frac{T}{P}\left(\frac{\partial Z}{\partial T}\right)_P = \frac{b}{RT} - \frac{2a}{RT^2} = \frac{1}{RT}\left(b - \frac{2a}{T}\right)$$

$$\frac{H-H^{ig}}{RT} = \frac{P}{RT}\left(b - \frac{2a}{T}\right)$$

b) $H - H^{ig} = 20\left(20 - \frac{80,000}{300}\right)$

$= -4,933$ cm^3 bar/mol $= -493$ J/mol K

c) $-\frac{T}{P}\left(\frac{\partial Z}{\partial T}\right)_P = \frac{1}{RT}\left(b - \frac{2a}{T}\right)$

$$-\left(\frac{Z-1}{P}\right) = -\frac{1}{RT}\left(b - \frac{a}{T}\right)$$

$$\frac{S-S^{ig}}{R} = \int_0^P -\frac{a}{RT^2}dP = -\frac{aP}{RT^2}$$

$S - S^{ig} = \frac{40,000(20)}{(300)^2} = 8.889$ cm^3 bar/mol K=0.889 J/mol K

(8.16) Using the Peng-Robinson equation, estimate the change in entropy

Solution :

From PREOS.xls

From State1, we have $S\text{-}S^{ig} = -82.519$; For State 2: $S\text{-}S^{ig} = -3.31335$

To calculate the state change for the ideal gas case,

$S_2^{ig} - S_1^{ig} = A\ln(T_2/T_1) + B(T2-T1) + C/2\,(T_2^2-T_1^2) + D/3(T_2^3-T_1^3) - R\ln(P_2/P_1)$

$= 7.3485$ J/mol K.

$S_2 - S_1 = -3.3133+7.3485+82.519 = 86.5$

From departure at State 1 =82.519/86.5 = 95%

From departure at State 2 =3.8%.

(8.17) Suppose we would like to establish limits for the rule $T_2 = T_1 (P_2 / P_1)^{R/Cp}$ ...

Solution: Use PREOS.xls

Using the short-cut vapor pressure equation and argon as a model fluid,

Psat = 0.0233MPa at T = 75.5 and sat Liq ref state at 0.1MPa gives S1 = 62.68. Steadily increasing the pressure till the error is more than 2K gives P=40 ⇒ Pr=8

Psat = 0.497 MPa at T = 105.7 and sat Liq ref state at 0.1MPa gives S1 = 63.057. Steadily increasing the pressure till the error is more than 2K gives P=3.7 ⇒ Pr=0.76

Evidently, this rule is better when you start from a low pressure. If you start from a reduced pressure above 0.1, you need to be more careful.

(8.18) A piston contains 2 moles of propane vapor at 425 K and 3.4 MPa...

Using a reference state of vapor at 400K and 0.1 MPa, the initial state is

Gas	T_c (K)	P_c (MPa)	ω	A	B	C	D
PROPANE	369.8	4.249	0.152	-4.224	3.06E-01	-1.59E-04	3.22E-08

Current State		Roots		Stable Root has a lower fugacity			
T (K)	425	Z	V	fugacity	H	U	S
P (MPa)	8.5		cm^3/gmol	MPa	J/mol	J/mol	J/molK
& for 1 root region		0.5111	212.456	5.0519	-5203.67	-7009.54	-44.7287

Final state

Current State		Roots		Stable Root has a lower fugacity			
T (K)	444	Z	V	fugacity	H	U	S
P (MPa)	3.4		cm^3/gmol	MPa	J/mol	J/mol	J/molK
& for 1 root region		0.82324	893.80	2.85322	2162.605	-876.308	-22.5166

$\Delta\underline{H} = 2(2162.6 + 5204) = 14733$ J

$\underline{Q} = \Delta\underline{U} - \underline{W} = 2(-876.3+7010) + 2000 = 14267$ J

(8.19) Vargaftik lists the following experimental values for the enthalpy departure function of isobutane at 175 C. Compute the theoretical values and their % deviations from experiment by a) generalized charts b) PREOS

		ω=0	ω=0.25	ω=0.17	Exp	Gen Chart		PREOS	
P	Pr	H-Hig	H-Hig	H-Hig	H-Hig	H-Hig	% Deviation	H-Hig	% Deviation
1.013	0.278	-0.25	-0.25	-16.06	-15.4	-16.1	4.2856891	-16.6	7.7922078
2.026	0.555	-0.5	-0.5	-32.12	-32.8	-32.1	2.0731944	-35.5	8.231707
3.546	0.972	-1.5	-1.5	-96.36	-64.72	-96.4	48.887479	-69.9	8.003708
7.091	1.944	-3.5	-3.5	-224.8	-177.5	-225	26.670392	-140	21.1493

(8.20) n-pentane is to be heated from liquid at 298 K and 0.01013 MPa...

Method 1) using reference state

$$\frac{H-H^{ig}}{RT} \text{ at ref} = \frac{-266.75}{(8.314)(310)} = -0.1035$$

State 1)

	stable root	less stable root
$H_1 =$	-27701 J/mol	-1457.7 J/mol
$H_2 =$	5613.9 J/mol	-17399 J/mol

$H_2 - H_1 = 5613.9 + 27701 = 33315$ J/mol

Method 2) without using reference state

State 1) $T_r = 0.634448$

$P_r = 0.030068$

$H - H^{ig} = -26526.4$ J/mol

$$\frac{H - H^{ig}}{RT} = -10.7066$$

State 2) $T_r = 0.7664$

$P_r = 0.0890$

$H - H^{ig} = -657.8$ J/mol

$$\frac{H - H^{ig}}{RT} = -0.2198$$

$\Delta H^{ig} = 120.1(360\text{-}298) = 7446.2$

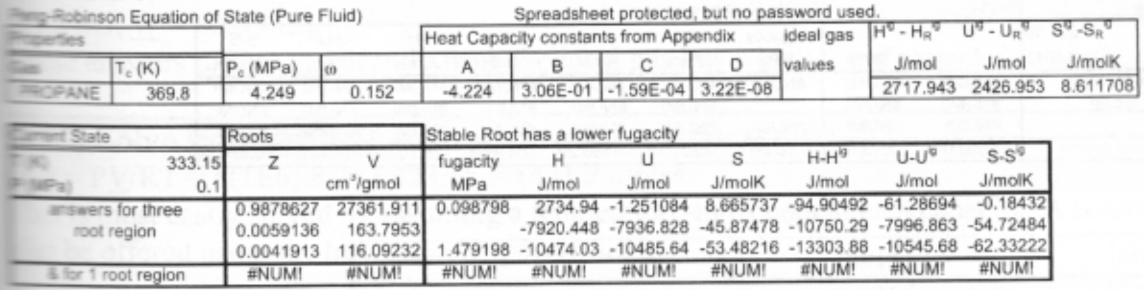
$-657.8 + 7446.2 + 26526.4 = 33315$ J/mol

(8.21) For each of the fluid state changes below, perform the following…

(i) Propane

(a) Using reference state as real vapor at 298.15 K and 0.1 MPa.($H_R = 0$)

Initial State



Peng-Robinson Equation of State (Pure Fluid)

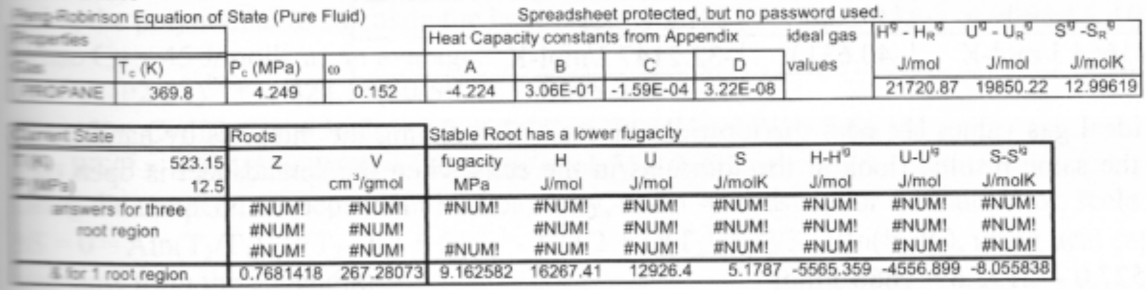
Spreadsheet protected, but no password used.

Properties				Heat Capacity constants from Appendix				ideal gas values	$H^{ig} - H_R^{ig}$	$U^{ig} - U_R^{ig}$	$S^{ig} - S_R^{ig}$
Gas	T_c (K)	P_c (MPa)	ω	A	B	C	D		J/mol	J/mol	J/molK
PROPANE	369.8	4.249	0.152	-4.224	3.06E-01	-1.59E-04	3.22E-08		2717.943	2426.953	8.611708

Stable Root has a lower fugacity

Current State		Roots Z	V cm^3/gmol	fugacity MPa	H J/mol	U J/mol	S J/molK	$H-H^{ig}$ J/mol	$U-U^{ig}$ J/mol	$S-S^{ig}$ J/molK
T (K)	333.15									
P (MPa)	0.1									
answers for three root region		0.9878627	27361.911	0.098798	2734.94	-1.251084	8.665737	-94.90492	-61.28694	-0.18432
		0.0059136	163.7953		-7920.448	-7936.828	-45.87478	-10750.29	-7996.863	-54.72484
		0.0041913	116.09232	1.479198	-10474.03	-10485.64	-53.48216	-13303.88	-10545.68	-62.33222
& for 1 root region		#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!

Final State



Peng-Robinson Equation of State (Pure Fluid)

Spreadsheet protected, but no password used.

Properties				Heat Capacity constants from Appendix				ideal gas values	$H^{ig} - H_R^{ig}$	$U^{ig} - U_R^{ig}$	$S^{ig} - S_R^{ig}$
Gas	T_c (K)	P_c (MPa)	ω	A	B	C	D		J/mol	J/mol	J/molK
PROPANE	369.8	4.249	0.152	-4.224	3.06E-01	-1.59E-04	3.22E-08		21720.87	19850.22	12.99619

Stable Root has a lower fugacity

Current State		Roots Z	V cm^3/gmol	fugacity MPa	H J/mol	U J/mol	S J/molK	$H-H^{ig}$ J/mol	$U-U^{ig}$ J/mol	$S-S^{ig}$ J/molK
T (K)	523.15									
P (MPa)	12.5									
answers for three root region		#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!
		#NUM!	#NUM!		#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!
		#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!
& for 1 root region		0.7681418	267.28073	9.162582	16267.41	12926.4	5.1787	-5565.359	-4556.899	-8.055838

(b)

	Initial	Final	Δ
V	27362 cm^3/mol	267.3	
H	2735 J/mol	16267.41	13.5 kJ/mol
S	8.6657 J/mol-K	5.1787	-3.487 J/mol-K

(c) We expect the change to be inaccurately calculated by the ideal gas assumption. The ideal gas values are near the top right of each spreadsheet, and in fact, the entropy change has the wrong sign. Calculating the integrals by hand would provide the same results. (look at the formulas in the cells when the spreadsheet is open on a computer).

$\Delta H^{ig} = 21720 - 2718 = 19.0$ kJ/mol
$\Delta S^{ig} = 12.9962 - 8.6117 = 4.3845$ J/mol-K

(ii) Methane:

(a) Reference State: Real vapor at 298.15K and 0.1 MPa, $H_R = 0$.

Initial State:

Properties				Heat Capacity constants from Appendix				ideal gas	$H^{ig} - H_R^{ig}$	$U^{ig} - U_R^{ig}$	$S^{ig} - S_R^{ig}$
Gas	T_c (K)	P_c (MPa)	ω	A	B	C	D	values	J/mol	J/mol	J/molK
Methane	190.6	4.604	0.011	19.25	5.21E-02	1.20E-05	-1.13E-08		-527.023	-402.313	-37.1355

Current State		Roots		Stable Root has a lower fugacity						
T (K)	283.15	Z	V	fugacity	H	U	S	$H-H^{ig}$	$U-U^{ig}$	$S-S^{ig}$
P (MPa)	7		$cm^3/gmol$	MPa	J/mol	J/mol	J/molK	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!
		#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!
& for 1 root region		0.8390507	282.17384	5.882944	-1919.99	-3895.21	-40.6313	-1411.1	-1032.21	-3.53818

Final State

Properties				Heat Capacity constants from Appendix				ideal gas	$H^{ig} - H_R^{ig}$	$U^{ig} - U_R^{ig}$	$S^{ig} - S_R^{ig}$
Gas	T_c (K)	P_c (MPa)	ω	A	B	C	D	values	J/mol	J/mol	J/molK
Methane	190.6	4.604	0.011	19.25	5.21E-02	1.20E-05	-1.13E-08		-2192.57	-1652.16	-8.3842

Current State		Roots		Stable Root has a lower fugacity						
T (K)	233.15	Z	V	fugacity	H	U	S	$H-H^{ig}$	$U-U^{ig}$	$S-S^{ig}$
P (MPa)	0.1013		$cm^3/gmol$	MPa	J/mol	J/mol	J/molK	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!
		#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!
& for 1 root region		0.9952189	19043.844	0.100817	-2201.15	-4130.29	-8.41664	-26.7099	-17.4422	-0.07483

(b)

	Initial	Final	Δ
V	19044 cm^3/mol	282.2	
H	-2201.2 J/mol	-1920.0	281.2 J/mol
S	-8.41664 J/mol-K	-40.6313	-32.2147 J/mol-K

(c) The ideal gas values are near the top right of each. Calculating the integrals by hand would provide the same results. (look at the formulas in the cells when the spreadsheet is open on a computer).

$\Delta H^{ig} = -527.0 - -2192.6 = 1666$ J/mol
$\Delta S^{ig} = -37.1355 - - 8.3842 = -28.75$ J/mol-K

(8.22) (Solution using spreadsheet) 1 m^3 of CO_2 initially at 150°C and 50 bar...

this is a closed system

a) $n = P\underline{V}/RT = 5(1E6)/8.314/423.15 = 1421.2$ moles

The final volume is $V^f = V^iP^i/P^f = 1(5/30) = 0.166\ m^3$

$\Delta\underline{U} = Q + W = 0$, $W = RT\ln(P^f/P^i) = 8.314(423.15)\ln(6) = 6303.5$ J/mol

Q = -6303.5 J/mol, W = 8.96 MJ, Q = -8.96 MJ

b) reference state 298K, 0.1MPa, H=0 for real gas.

(ref state does not matter, values for H,U,S may differ but not change)

Gas	T_c (K)	P_c (MPa)	ω	A	B	C	D
CARBON DIOXIDE	304.2	7.382	0.228	19.8	7.34E-02	-5.60E-05	1.72E-08

Current State		Roots		Stable Root has a lower fugacity			
T (K)	423.15	Z	V	fugacity	H	U	S
P (MPa)	5		cm^3/gmol	MPa	J/mol	J/mol	J/molK
& for 1 root region		0.921	647.68	4.61	3858.3	619.8819	-20.6005

n = V/V = 1E6/647.68 = 1544 moles

final state is also at 423.15K

Current State		Roots		Stable Root has a lower fugacity			
T (K)	423.15	Z	V	fugacity	H	U	S
P (MPa)	30		cm^3/gmol	MPa	J/mol	J/mol	J/molK
& for 1 root region		0.7851	92.0676	20.54	-901.961	-3663.99	-44.279

V = 1544*92.07 = 0.142 m^3

The energy balance gives, ΔU = Q + W = -3664 –620 = -4284 J/mol (which is non-zero!). Work is tedious to calculate by the integral -∫PdV, but we may find Q using the entropy balance: TΔS = Q = 423.15(-23.6785) = -10020 J/mol, therefore W = ΔU – Q = -4284 +10020 = 5736 J/mol. Q = -15.5 MJ, W = 8.86 MJ.

These answers differ significantly from the ideal gas law which is not expected to apply.

(8.23) Solve problem 8.22 for an adiabatic compression.

a) n = PV/RT = 5(1E6)/8.314/423.15 = 1421.2 moles

This is most easily solved by assuming a temperature-independent heat capacity. A solution will also be offered using the heat capacity polynomial.

Assuming a constant heat capacity:

Using the polynomial to calculate the heat capacity at 423.15, Cp = 42.14, at 600 K, Cp = 47.4, so use Cp = 45 J/molK as an average.

$T2 = T1(P2/P1)^{R/Cp} = 423.15(30/5)^{8.314/45} = 589.2$ K

W = ΔU = Cv(T2-T1) = 36.7(589.2-423.15) = 6094 J/mol, W = 8.66 MJ

V^f = RT/P = 8.314(589.2)/30 = 163.2 cm^3/mol, V = 0.232 m^3.

Using the temperature dependent heat capacity, and a spreadsheet or the calculator, seek:

$\Delta S = 0 = A\ln(T_2/T_1)+B(T_2 - T_1) + C(T_2^2 - T_1^2)/2 + D(T_2^3 - T_1^3)/3 - R\ln(P_2/P_1)$, using heat capacity constants from the appendix,

T^f = 590.7, V^f = 163.7 cm^3/mol, V = 0.233

W = ΔU = ΔH – RΔT, using heat capacity polynomial,

$\Delta H = A(T2-T1) + B(T2^2 - T1^2)/2 + C(T2^3 - T1^3)/3 + D(T2^4 - T1^4)/4$ =7505.6 J/mol,

ΔU = 7505.6 – 8.314(590.7 – 423.15) = 6112 J/mol, W = 8.68 MJ

b) reference state 298K, 0.1MPa, H=0 for real gas.

Gas	T_c (K)	P_c (MPa)	ω	A	B	C	D
CO2	304.2	7.382	0.228	19.8	7.34E-02	-5.60E-05	1.72E-08

Current State		Roots		Stable Root has a lower fugacity			
T (K)	423.15	Z	V	fugacity	H	U	S
P (MPa)	5		cm^3/gmol	MPa	J/mol	J/mol	J/molK
& for 1 root region		0.921	647.68	4.61	3858.3	619.8819	-20.6005

$n = \underline{V}/V = 1E6/647.68 = 1544$ moles

The final state will have the same entropy. Using goal seek or solver to adjust T:

Current State		Roots		Stable Root has a lower fugacity			
T (K)	611.28	Z	V	fugacity	H	U	S
P (MPa)	30		cm^3/gmol	MPa	J/mol	J/mol	J/molK
& for 1 root region		1.0098	171.07047	29.18278	11107.74	5975.623	-20.6005

$V^f/V^i = 171.07/647.7 = 0.264$, $\underline{V}^f = 0.264$ m^3

$W = \Delta U = 5976 - 619.8 = 5356$ J/mol, $\underline{W} = 8.27$ MJ

Note: The temperature goes up enough that the ideal gas law isn't too far off for a first guess, but this result should not be over-generalized.

(8.24)Consider problem statement 3.11 using benzene...

overall E-bal $\Delta\underline{U} = -\int P_{applied} d\underline{V} = -P_{applied}\Delta\underline{V}$

reference state: H=0 for real liquid at 298K, 1 bar.

Gas	T_c (K)	P_c (MPa)	ω	A	B	C	D
BENZENE	562.2	4.898	0.211	-33.92	4.74E-01	-3.02E-04	7.13E-08

Current State		Roots		Stable Root has a lower fugacity			
T (K)	673	Z	V	fugacity	H	U	S
P (MPa)	2		cm^3/gmol	MPa	J/mol	J/mol	J/molK
& for 1 root region		0.912	2550.821	1.832	80033.15	74931.51	167.9306

$\underline{U}^i = 74932$ J

$\underline{V}_{tank} = 2551$ cm^3

Tank will have the entropy as the initial state with P = 0.7.

Current State		Roots		Stable Root has a lower fugacity			
T (K)	634.43188	Z	V	fugacity	H	U	S
P (MPa)	0.7		cm^3/gmol	MPa	J/mol	J/mol	J/molK
& for 1 root region		0.962	7252.486	0.674	74671.47	69594.73	167.9306

$n_{tank} = 2551/7252 = 0.352$ moles, $n_{cyl} = 1 - 0.352 = 0.648$

$\underline{U}^f_{tank} = 0.352(69595) = 24497$ J

E-balance, $\Delta\underline{U} = \underline{U}^f_{cyl} + \underline{U}^f_{tank} - \underline{U}^i = -0.7(\underline{V}^f_{cyl} - 0)$,

$0.648(U^f_{cyl} + 0.7\, V^f_{cyl}) + 24497 - 74932 = 0$. Setting this up as an objective function on the spreadsheet, we can solve for T at 0.7 MPa.

Current State		Roots		OBJ FUNC=	0		
T (K)	653.37	Z	V	fugacity	H	U	S
P (MPa)	0.7		cm^3/gmol	MPa	J/mol	J/mol	J/molK

& for 1 root region	0.966	7496.444	0.677	77831.79	72584.28	172.8388

Note: some of the difference between this problem and the problem from Chap 3 is the heat capacity, so the vapor phase non-ideality is only part of the difference.

(8.25) Solve problem 8.24 using n-pentane…

overall E-bal $\Delta \underline{U} = -\int P_{applied} d\underline{V} = -P_{applied} \Delta \underline{V}$

reference state: H=0 for real liquid at 298K, 1 bar.

Gas	T_c (K)	P_c (MPa)	ω	A	B	C	D
n-PENTANE	469.7	3.369	0.249	-3.626	4.87E-01	-2.58E-04	5.31E-08

Current State		Roots		Stable Root has a lower fugacity			
T (K)	673	Z	V	fugacity	H	U	S
P (MPa)	2		cm^3/gmol	MPa	J/mol	J/mol	J/molK
& for 1 root region		0.939	2628.144	1.879	91092.07	85835.78	196.8026

$\underline{U}^i = 85835$ J; $\underline{V}_{tank} = 2628$ cm^3

Tank will have the entropy as the initial state with P = 0.7.

Current State		Roots		Stable Root has a lower fugacity			
T (K)	643.89	Z	V	fugacity	H	U	S
P (MPa)	0.7		cm^3/gmol	MPa	J/mol	J/mol	J/molK
& for 1 root region		0.974	7445.636	0.682	85586.15	80374.2	196.8026

$n_{tank} = 2628/7446 = 0.353$ moles, $n_{cyl} = 1 - 0.353 = 0.647$

$\underline{U}^f_{tank} = 0.353(80374) = 28372$ J

E-balance, $\Delta \underline{U} = \underline{U}^f_{cyl} + \underline{U}^f_{tank} - \underline{U}^i = -0.7(\underline{V}^f_{cyl} - 0)$,

$0.647(U^f_{cyl} + 0.7\ V^f_{cyl}) + 28372 - 85835 = 0$. Setting this up as an objective function on the spreadsheet, we can solve for T at 0.7 MPa.

Current State		Roots		OBJ FUNC=		0	
T (K)	658.53	Z	V	fugacity	H	U	S
P (MPa)	0.7		cm^3/gmol	MPa	J/mol	J/mol	J/molK
& for 1 root region		0.976	7632.753	0.683	88814.53	83471.6	201.7602

Note: some of the difference between this problem and the problem from Chap 2 is the heat capacity, so the vapor phase non-ideality is only part of the difference.

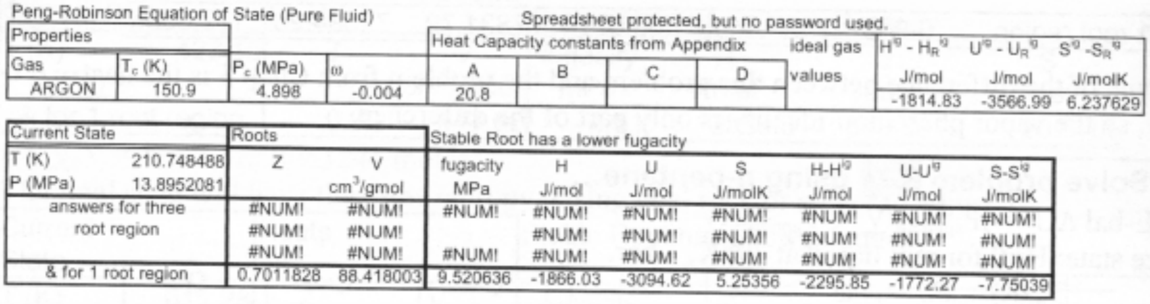
(8.26) A tank is divided into two equal halves by an internal…

a. The temperature stays the same, and the pressure drops to 350 bar.

b. Choosing initial state as reference state and setting H=0 at ref state, $U^i = -3094.6$ J/mol. Taking the boundary around the entire tank, the energy balance gives $U^f = U^i$. By material balance, $V^f = 2*V^i$, and $V^i = 44.209$ cm3/mol.

Therefore, search for the state where Uf = -3094.6 J/mol, and Vf = 88.418 cm3/mol. We may use solver to adjust P,T to find Uf = -3094.6 J/mol subject to the constraint that Vf = 88.418 cm3/mol.

The answer is 210.7 K and 13.9 MPa:



Peng-Robinson Equation of State (Pure Fluid) Spreadsheet protected, but no password used.

Properties				Heat Capacity constants from Appendix				ideal gas values	$H^{ig} - H_R^{ig}$	$U^{ig} - U_R^{ig}$	$S^{ig} - S_R^{ig}$
Gas	T_c (K)	P_c (MPa)	ω	A	B	C	D		J/mol	J/mol	J/molK
ARGON	150.9	4.898	-0.004	20.8					-1814.83	-3566.99	6.237629

Current State		Roots		Stable Root has a lower fugacity						
T (K)	210.748488	Z	V	fugacity	H	U	S	$H-H^{ig}$	$U-U^{ig}$	$S-S^{ig}$
P (MPa)	13.8952081		cm^3/gmol	MPa	J/mol	J/mol	J/molK	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!
		#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!
& for 1 root region		0.7011828	88.418003	9.520636	-1866.03	-3094.62	5.25356	-2295.85	-1772.27	-7.75039

(8.27)The divided tank of the preceding problem develops a leak instead...

SOLUTION: (basis 1 mole argon total) Use PREOS.xls. Let "1" be the side that is initially at high pressure. System is both sides together

$E-BAL \quad N_1^i U_1^i = N_1^f U_1^f + N_2^f U_2^f$ S-BAL $\underline{S}_1^f = \underline{S}_1^i$ $\quad \dot{\underline{S}}_{gen} \neq 0$, but assume no entropy generated on "1" side

Must guess P_1^f then apply the S-bal on side 1, then M-bal overall, then E-bal overall to check the results of the P^f guess.

At the initial state (Using real vapor ref state at 298K and 1 bar, $H_R = 0$)

At the initial state, $Z_1^i = 1.249$ $U_1^i = -5330.06$ J/mol, $S_1^i = -61.2088$, $\underline{V}_1^i = Z_1^i n_1^i RT_1^i / P_1^i = 1.249*1*8.314*298/70 = 44.207$ cm^3

Noting $S_1^f = -61.2088$, guess $P_1^f = 200$ bar

Guess T_1^f to match $S_1^f \Rightarrow T_1^f = 209.45$ K, $Z_1^f = 0.7037$, $U_1^f = -5988.2$ J/mol

$$\text{M-bal. } n_1^f = \frac{20(44.207)}{0.7037(8.314)(209.45)} = 0.7215,\ n_2^f = 0.2785$$

$$\Rightarrow Z_2^f T_2^f = \frac{P_2^f \underline{V}_2}{n_2^f R} = \frac{20(44.207)}{(0.2785)8.314} = 381.84;$$ Guess T_2^f till product $Z_2^f T_2^f$ is $381.84 \Rightarrow T_2^f = 382$,

where $Z_2^f = 0.999$, $U_2^f = -2307.6$

Overall E-bal.

$0.7215*(-5988.2) + 0.2785*(-2307.6) = -4963 \neq -5330.06$

2nd Guess $P_f = 170$ bar, to match S, find $T_1^f = 200.8$K

$\Rightarrow Z_1^f = 0.6504$, $U_1^f = -6036$ J/mol

$$\text{M-bal. } n_1^f = \frac{17*44.207}{0..6920*8.314*200.8} = 0.6920 \Rightarrow n_2^f = 0.3080$$

$$\Rightarrow Z_2^f T_2^f = \frac{P_2^f \underline{V}_2}{n_2^f R} = \frac{17(44.207)}{(0.3080)8.314} = 293.46;$$ Guess T_2^f till product $Z_2^f T_2^f$ is $293.46 \Rightarrow T_2^f = 312$,

where $Z_2^f = 0.9406$, $U_2^f = -3336$

Overall E-bal.

$0.6920*(-6036) + 0.3080*(-3336) = -5204 \sim -5330$ close enough!

$P_f = 170$ bar, $T_1^f = 200.8$ K$\Rightarrow T_2^f = 312$ K

The real fluid is VERY different from the ideal gas.

(8.28) A practical application closely related to the above problem...

Use PREOS.xls. Ref = satL at 0.1MPa. 250g/44g/mole=5.68moles

10bars = 300K$\Rightarrow$S = 27.88 = q(SV)+(1-q)SL at 0.85MPa

=> 27.88 = q(77)+(1-q)25.03⇒*q*=0.055

⇒V = .055(2391)+.945(84) = 211cc/gmol ⇒500cc/211cc/gmol = 2.38moles ⇒3.3 moles gone to tire. Moles in tire = 40000*0.1/(8.314*298) + 3.3 = 4.914

P = 8.314*300/(40000/4.914) = 0.3MPa = 30psig. So it's OK.

If remaining 2.38 moles goes to tire (~neglecting gas left in can), ~4moles in tire

⇒ P = 8.314*300/(40000/4) = 0.25 MPa = 21 psig. So it's OK for 2.

(8.29) Ethylene at 30bar and 100°C passes through a throttling valve...

E-Bal: $\Delta H = Q + W$ and $W = 0$

T_c = 282.4K, P_c= 50.36 bar, ω= 0.085, T_b= 169.4K

Appendix B ⇒ A=3.806; B=.1566; C=-8.348E-5; D=1.755E-8

$C_p(400)$ = 54 J/mol-K (Note: you get 44 J/mole-K from Cp(298))

T=373, P=30 bars ⇒ T_r=1.3208; P_r=0.5957

T=423, P=20 bars ⇒ T_r=1.4979; P_r=0.3971

Using the heat capacity at 400K as an average,

by departures on spreadsheet:

$$\Delta H = [(-.1521)423 + 6.52(50) + (.3287)373]8.314 = \boxed{3197\text{ J/mol}}$$

SOLUTION: using spreadsheet, reference state 298K, 1 bar, H = 0 for real vapor.

Inlet Gas	T_c (K)	P_c (MPa)	ω	A	B	C	D
ETHYLENE	282.4	5.032	0.085	3.806	1.57E-01	-8.35E-05	1.76E-08

Current State		Roots		Stable Root has a lower fugacity			
T (K)	373.15	Z	V	fugacity	H	U	S
P (MPa)	3		cm^3/gmol	MPa	J/mol	J/mol	J/molK
& for 1 root region		0.903	933.903	2.721	2603.26	-198.449	-19.4267

Outlet

Current State		Roots		Stable Root has a lower fugacity			
T (K)	423.15	Z	V	fugacity	H	U	S
P (MPa)	2		cm^3/gmol	MPa	J/mol	J/mol	J/molK
& for 1 root region		0.958	1685.600	1.917	5788.316	2417.117	-8.26273

The throttle valve doesn't change the enthalpy.

$$Q = \Delta H = 5788 - 2603 = \boxed{3185\text{ J/mol}}$$

(8.30) In the final stage of a multistage, adiabatic compression...

reference state: H=0 for real vapor at 298K and 1 bar.

Gas	T_c (K)	P_c (MPa)	ω	A	B	C	D
METHANE	190.6	4.604	0.011	19.25	5.21E-02	1.20E-05	-1.13E-08

Current State		Roots		Stable Root has a lower fugacity			
T (K)	198.15	Z	V	fugacity	H	U	S
P (MPa)	2		cm^3/gmol	MPa	J/mol	J/mol	J/molK
& for 1 root region		0.840	691.936	1.715	-3994.97	-5378.84	-40.6225

Outlet (reversible) adjust T to match S

Current State		Roots		Stable Root has a lower fugacity

T (K)	271.66	Z	V	fugacity	H	U	S
P (MPa)	6		cm^3/gmol	MPa	J/mol	J/mol	J/molK
& for 1 root region		0.835	314.406	5.046	-2214.75	-4101.19	-40.6225

$\Delta H = \Delta H'/\eta = (-2214.8 + 3995)/0.76 = 1780.2/0.76 = 2342$ J/mol

$H^{out} = -3995 + 2342 = -1653$ J/mol

Oulet (actual) adjust T to match H

Current State		Roots		Stable Root has a lower fugacity			
T (K)	284.55	Z	V	fugacity	H	U	S
P (MPa)	6		cm^3/gmol	MPa	J/mol	J/mol	J/molK
& for 1 root region		0.861	339.383	5.174	-1653	-3689.3	-38.602

The actual T is 285 vs. the reversible outlet T of 272K. W = ΔH= 2342 J/mol

(8.31) (a) Ethane is compressed from 280 K and 1 bar to 310 K and 75 bar

a) Compute the change in enthalpy per mole given $C_P/R = 5$

Changes in enthalpy is independent of reference state and so,

$$\Delta H = (H - H^{ig})_{T_2,P_2} + \int_{T1}^{T2} C_P dT - (H - H^{ig})_{T_1,P_1}$$

From the table generated from PREOS.XLS file for ethane(see table below), we have

$\Delta H = -9078.73 + 5*8.314*(310 - 280) - (-63.9801) = -7767.65$ J/mol

b) Ethane is isentropically expanded from 75 bar and 310K to 1 bar,

If we try to set the outlet entropy equal to the inlet entropy (-57.015, see table below), the root that gives the same entropy (not shown) isn't the stable root! Therefore, the outlet must be in the two-phase region.

To find out the saturation temperature we adjust the T at 1 bar to get the value of fugacity ratio equal to 1. Using the solver function of Excel with the at P = 1 bar we get $T_2 = 184.21$ K. The saturated vapor value of entropy (-21.28) is larger than the inlet entropy, therefore the outlet IS in the two phase region. Using the saturation values for entropy in the same way as we did from property tables,

$$S_1 = S_2 = S_2^L + q(S_2^V - S_2^L)$$

$-57.015 = S_2 = -100.93 + q(-21.28 + 100.93) \Rightarrow q = 0.5513$

The departure function for state 2 then would be

$(H-H^{ig})_2 = -14788 + 0.5513(-115.4 + 14788) = -6699$ J/mol

Writing the enthalpy balance

$$\Delta H = (H - H^{ig})_{T_2,P_2} + \int_{T_1}^{T_2} C_P dT - (H - H^{ig})_{T_1,P_1}$$

We get

$\Delta H = -6699 + 5*8.314*(184.21 - 310) - (-9078.73) = -2849.36$ J/mol

Since for an isentropic process $\Delta H = W_S$ we have the work per mole from the turbine = - 2849.36 J/mol

The quality is pretty low, and the expander should probably be redesigned for a higher quality outlet.

Peng-Robinson Equation of State (Pure Fluid)

Properties				Heat Capacity constants from Appendix				ideal gas	$H^{ig} - H_R^{ig}$	$U^{ig} - U_R^{ig}$	$S^{ig} - S_R^{ig}$
Gas	T_c (K)	P_c (MPa)	ω	A	B	C	D	values	J/mol	J/mol	J/molK
ETHANE	305.4	4.88	0.099						-923.289	-3251.21	-3.19499

Properties of interest are given in different colored fonts

Current State		Roots		Stable Root has a lower fugacity								
T (K)	280	Z	V	fugacity	H	U	S	$H-H^{ig}$	$U-U^{ig}$	$S-S^{ig}$	T_r	0.91683
P (MPa)	0.1		$cm^3/gmol$	MPa	J/mol	J/mol	J/molK	J/mol	J/mol	J/molK	P_r	0.020492
answers for three root region		#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!		
		#NUM!	#NUM!		#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!		
		#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!		
& for 1 root region		0.990034	23047.2	0.099011	-928.873	-3233.59	-3.21433	-63.9801	-40.7805	-0.14588		

Current State		Roots		Stable Root has a lower fugacity								
T (K)	310	Z	V	fugacity	H	U	S	$H-H^{ig}$	$U-U^{ig}$	$S-S^{ig}$	T_r	1.015062
P (MPa)	7.5		$cm^3/gmol$	MPa	J/mol	J/mol	J/molK	J/mol	J/mol	J/molK	P_r	1.536885
answers for three root region		#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!		
		#NUM!	#NUM!		#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!		
		#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!		
& for 1 root region		0.276874	95.14651	3.673957	-8379.73	-9093.33	-57.0148	-9078.73	-7214.99	-23.3531		

Current State		Roots		Stable Root has a lower fugacity						
T (K)	184.2057	Z	V	fugacity	H	U	S	H-Hig	U-Uig	S-Sig
P (MPa)	0.1		cm3/gmol	MPa	J/mol	J/mol	J/molK	J/mol	J/mol	J/molK
answers for three root region		0.969765	14851.82	0.097058	-5106.1	-6591.28	-21.2756	-115.396	-69.0917	-0.37818
		0.024281	371.8579		-8996.59	-9033.77	-56.4115	-4005.89	-2511.59	-35.5141
		0.003311	50.70263	0.097058	-19778.5	-19783.6	-100.928	-14787.8	-13261.4	-80.0306
& for 1 root region		#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!

(8.32) Our space program requires a portable engine..

Tc = 2300K, Pc = 19.5MPa, w = 0, Cp = 2.5R

The stream numbers will be those of Figure 5.1

Reference State		For real fluid	Roots					
T (K)	1200	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	0.990186	98788.86	0.099027	-229.53	-131.616	-0.11001
0			0.008124	810.5447				
0 for ig, 1 for real fluid ref		2	0.000925	92.31107	0.146141	-101390	-91422.9	-87.634
0		3	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!

Identifier Index for reference state row to use from Row 9 - Row 12 (Enter 1, 2, or 3)
YOU MUST CHOOSE A ROW WITH CALCULABLE NUMBERS, NOT ONE WITH #NUM!

1

The outlet of the boiler is at 1444 K and 0.828 MPa

Current State		Roots		Stable Root has a lower fugacity			
T (K)	1444	Z	V	fugacity	H	U	S
P (MPa)	0.828		$cm^3/gmol$	MPa	J/mol	J/mol	J/molK
answers for three root region		0.9457596	13712.847	0.785212	3499.113	-7855.12	-14.3751
		0.0421201	610.71138		-25073	-25578.7	-43.9573
		0.0068588	99.447258	0.785164	-91059.4	-91141.7	-79.8583
& for 1 root region		#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!

H_3 = 3.499 kJ/mol, S_3 = -14.3751 J/mol-K

The outlet of the turbine will be a mixture of saturated vapor and liquid

Current State		Roots		Stable Root has a lower fugacity			
T (K)	1157	Z	V	fugacity	H	U	S
P (MPa)	0.1013		cm^3/gmol	MPa	J/mol	J/mol	J/molK
answers for three root region		0.9891626	93929.416	0.100213	-1137.04	-10652.1	-0.98643
		0.0090727	861.52787		-24424.3	-24511.5	-43.0719
		0.0009613	91.286887	0.099862	-103138	-103147	-89.1168
& for 1 root region		#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!

a) The quality will be determined by matching the inlet entropy for the reversible turbine

$S_4 = -14.3751 = -89.1168 + q\,(-0.98643 + 89.1168) \Rightarrow q = 0.848$

the work output

$H_4 = -103138 + 0.848\,(-1137 + 103138) = -16640$ J/mol

$W_S = H_4 - H_3 = -16640 - 3499 = -20.14$ kJ/mol

$Q_H = H_3 - H_6 \approx H_3 - H_5 = 3499 - (-103138) = 106.6$ kJ/mol

$\eta = -W_S/Q_H = 20.14/106.6 = 0.189$

For a Carnot Cycle $\eta = 1 - T_L/T_H = 1 - 1156/1444 = 0.1994$

The efficiency is close to the Carnot value. Refer back to the Figure 5.1. We approach the Carnot cycle for points 2, 3, and 4 of the Figure, but need a special turbine to do so.

(8.33) Find the minimum shaft work(in kW) necessary...

n-butane liquefaction.

Inlet vapor at 0.1 MPa, 290 K, outlet liq. at 0.1 MPa, 265 K

$$0 = S^{out}\dot{n}^{out} - S^{in}\dot{n}^{in} + \frac{\dot{\underline{Q}}}{T}$$

Ref. State: T_R =300 K, P_R =0.1 MPa vapor root

PREOS.xls

	H(kJ/mol)	S (kJ/mol K)
inlet 290 K	−984.4	−3.337
outlet 265 K	−25882	−94.764

Entropy balance

$$\dot{\underline{Q}} = 12\left(\frac{mol}{\text{min}}\right)(-94.764 + 3.337)(298) = -327\,\text{kJ/min}$$

Energy balance

$$0 = H^{in}\dot{n}^{in} - H^{out}\dot{n}^{out} + \dot{\underline{Q}} + \dot{\underline{W}}_S$$

$$\Delta H\dot{n} - \dot{\underline{Q}} = \dot{\underline{W}}_S = \frac{(-25882 + 984.4)(12)}{1000} + 327\left(\frac{kJ}{\text{min}}\right) = 28.2\text{ kJ/min; } 28.2 / 60\text{ sec} = 0.47\text{ kW}$$

(8.34) The enthalpy of normal liquids changes nearly linearly...

Below is a tabulation.

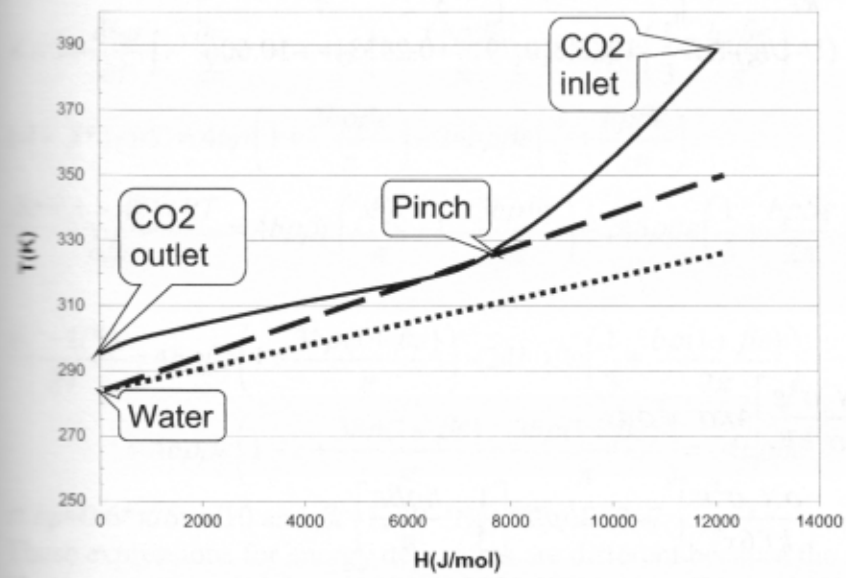
T	P	H	S	U	FUG
K	MPa	J/mol	J/molK	J/mol	MPa
388.15	8.6	12023	37.054	9404.8	7.0777
380	8.6	11550	35.824	9044.9	6.959

370	8.6	10950	34.223	8589.5	6.7993
360	8.6	10319	32.493	8112.5	6.6219
350	8.6	9641.6	30.585	7602.8	6.4237
340	8.6	8891.8	28.411	7039.6	6.2005
330	8.6	8009.7	25.776	6375.9	5.9454
320	8.6	6806.1	22.068	5459.2	5.6451
310	8.6	3668.4	12.068	2889.6	5.2482
300	8.6	811.1	2.7251	283.08	4.656
295.15	8.6	0	5.52E-09	-485.08	4.3428

a) plot is shown. The enthalpy of CO2 decreases slowly with T at first, then more rapidly. This creates a non-linear temperature profile.

b) a pinch point develops if the water outlet is raised to about 345K.

the highest outlet temperature that assures the desired ΔT is about 325K.



(8.35) An alternative to the pressure equation route from the molecular...

Solution

$$U - U^{id} = \frac{N_A\rho}{2}\int_0^\infty N_A u g 4\pi r^2 dr$$

$$g = 1 + \frac{\rho N_A}{r^3 kT}\sigma^6\varepsilon$$

Square Well Fluid

$$u = \infty \quad \sigma \ge r$$
$$= -\varepsilon \quad \sigma \le r \le 1.5\sigma$$
$$= 0 \quad r \ge 1.5\sigma$$
$$x = r/\sigma$$
$$\sigma dx = dr$$
$$U - U^{id} = -\frac{N_A\rho}{2}\int_{\sigma}^{1.5\sigma} N_A\varepsilon\left[1 + \frac{\rho N_A\sigma^6\varepsilon}{r^3kT}\right]4\pi r^2 dr$$
$$U - U^{id} = -\frac{N_A\rho}{2}\int_{1}^{1.5} N_A\varepsilon\left[1 + \frac{\rho N_A\sigma^6\varepsilon}{x^3\sigma^3kT}\right]4\pi x^2\sigma^2 dx$$
$$\frac{U - U^{id}}{RT} = -\frac{4\pi N_A\rho\sigma^3\varepsilon}{2kT}\left[\frac{x^3}{3} + \frac{\rho N_A\sigma^3\varepsilon}{kT}\ln x\right]_1^{1.5} = -12b\rho\beta\varepsilon\left[\frac{1.5^3 - 1}{3} + \frac{6b\rho\beta\varepsilon}{\pi}\ln 1.5\right]$$

at $b\rho$ =0.6*π/6=π/10 and $\beta\varepsilon$=1, $(U\text{-}Uig)/RT = -10.248[0.7917+0.2433] = -10.606$

b) Sutherland Potential

$u(r) = \propto \quad r \le \sigma$
$\quad = -\varepsilon(\sigma/r)^6 \quad r > \sigma$
$x = r/\sigma \qquad \sigma dx = dr$

At $r = \sigma$ x=1 At $r = \propto$ $x = \propto$.
$$U - U^{id} = -\frac{N_A\rho}{2}\int_{1}^{\infty}\frac{N_A\varepsilon}{x^6}\left[1 + \frac{\rho N_A\sigma^3\varepsilon}{x^3\sigma^3kT}\right]4\pi\sigma^2x^2\sigma dx$$
$$\frac{U - U^{id}}{RT} = -\frac{N_A\,\rho 4\pi\sigma^3\varepsilon}{2kT}\left[-\frac{1}{3x^3} - \frac{\rho N_A\sigma^3\varepsilon}{kT6x^6}\right]_1^{\infty} = -12b\rho\beta\varepsilon\left[\frac{1}{3} + \frac{b\rho\beta\varepsilon}{\pi}\right]$$
at $b\rho$=0.6*π/6=π/10 and $\beta\varepsilon$=1, $(U\text{-}Uig)/RT = -10.248[0.3333+0.1000] = -4.441$

(8.36) Evaluate the internal energy departure function at $\rho N_A\sigma^3$=0.6 and ε/kT=1 …

(a) SW fluid $Z = 1+4\pi\,\rho N_A\sigma^3/6\,\{g(\sigma) - R^3[1\text{-}\exp(-\varepsilon/kT)]g(1.5\sigma)\}$
$Z = 1+4\,b\rho\{1+(6/\pi)\,b\rho\,\varepsilon/kT - R^3Y/(Y+1)\,{*}(1+0.3{*}6/\pi\,b\rho\,\varepsilon/kT)\,\}$
$(A\text{-}Aig)/RT = 4\{b\rho + (3/\pi)\,(b\rho)^2\,\varepsilon/kT - 1.5^3Y/(Y+1){*}[\,b\rho + 0.9/\pi\,(b\rho)^2\,\varepsilon/kT]\}$
$\beta \equiv 1/kT \Rightarrow (U\text{-}Uig)/RT = \beta\varepsilon\partial(A\text{-}Aig/RT)/\partial(\beta\varepsilon)$
$$\frac{\beta\varepsilon\partial(A - A^{ig})/RT}{\partial\beta\varepsilon} = \frac{12(b\rho)^2\beta\varepsilon}{\pi} - \frac{4{*}1.5^3Y}{(Y+1)}\left[\frac{0.9(b\rho)^2\beta\varepsilon}{\pi} + \left(1 - \frac{Y}{(Y+1)}\right)\frac{\beta\varepsilon\partial Y}{Y\partial\beta\varepsilon}\left(b\rho + \frac{0.9(b\rho)^2\beta\varepsilon}{\pi}\right)\right]$$
$$\frac{\beta\varepsilon\partial Y}{Y\partial\beta\varepsilon} = \frac{\beta\varepsilon(Y+1)}{Y};\ \left(1 - \frac{Y}{(Y+1)}\right) = \frac{1}{(Y+1)}$$

$$\frac{(U-U^{ig})}{RT}=\frac{12(b\rho)^2\beta\varepsilon}{\pi}-\frac{4*1.5^3\beta\varepsilon}{(Y+1)}\left[\frac{0.9(b\rho)^2 Y}{\pi}+\left(b\rho+\frac{0.9(b\rho)^2\beta\varepsilon}{\pi}\right)\right]$$

$$\frac{(U-U^{ig})}{RT}=\frac{12(b\rho)^2\beta\varepsilon}{\pi}-\frac{4*1.5^3\beta\varepsilon}{(Y+1)}\left[b\rho+\frac{0.9(b\rho)^2(Y+\beta\varepsilon)}{\pi}\right]$$

at $b\rho=0.6*\pi/6=\pi/10$ and $\beta\varepsilon=1$, $(U\text{-}U^{ig})/RT = 0.3770 - 4.9664[\pi/10+0.3910] = -3.1252$

(b) For the Sutherland Potential (u=-ε/x^6), split the P-eqn integral to (0,σ) and (σ^+, ∞). For (0,σ), the result is the same as the SW potential, ie. $4b\rho g(\sigma)$. For (σ^+, ∞),

$$\int_{\sigma}^{\infty} r\frac{du}{dr}g(r)4\pi r^2 dr = 6\varepsilon\sigma^3\int_1^{\infty}\frac{1}{x^6}g(r)4\pi x^2 dx = 6\varepsilon\sigma^3\int_1^{\infty}\frac{1}{x^6}\left(1+\frac{6b\rho\beta\varepsilon}{\pi x^3}\right)4\pi x^2 dx$$

$$=24\pi\varepsilon\sigma^3\int_1^{\infty}\left(\frac{1}{x^4}+\frac{6b\rho\beta\varepsilon}{\pi x^7}\right)dx = -24\pi\varepsilon\sigma^3\left(\frac{1}{3x^3}+\frac{b\rho\beta\varepsilon}{\pi x^6}\right)_1^{\infty} = 24\pi\varepsilon\sigma^3\left(\frac{1}{3}+\frac{b\rho\beta\varepsilon}{\pi}\right)$$

$$Z=1-\frac{4b\rho}{kT}\int r^3\frac{du}{dr}dr = 1+4b\rho\left(1+\frac{6b\rho\beta\varepsilon}{\pi}\right)-24b\rho\beta\varepsilon\left(\frac{1}{3}+\frac{b\rho\beta\varepsilon}{\pi}\right)$$

$$(A-A^{ig})/RT = 4b\rho\left(1+\frac{3b\rho\beta\varepsilon}{\pi}\right)-24b\rho\beta\varepsilon\left(\frac{1}{3}+\frac{b\rho\beta\varepsilon}{2\pi}\right)$$

$$\frac{\beta\varepsilon\partial(A-A^{ig})/RT}{\partial\beta\varepsilon}=4b\rho\beta\varepsilon\left(\frac{3b\rho}{\pi}+1+\frac{3b\rho\beta\varepsilon}{\pi}\right)-24b\rho\beta\varepsilon\left(\frac{1}{3}+\frac{b\rho\beta\varepsilon}{2\pi}+\frac{b\rho}{2\pi}\right)$$

$$\frac{(U-U^{ig})}{RT}=4b\rho\beta\varepsilon\left(1+\frac{3b\rho(1+\beta\varepsilon)}{\pi}\right)-24b\rho\beta\varepsilon\left(\frac{1}{3}+\frac{b\rho(1+\beta\varepsilon)}{2\pi}\right)$$

$$=4b\rho\beta\varepsilon\left(1-2+\frac{3b\rho(1+\beta\varepsilon)}{\pi}-\frac{3b\rho(1+\beta\varepsilon)}{\pi}\right)=-4b\rho\beta\varepsilon$$

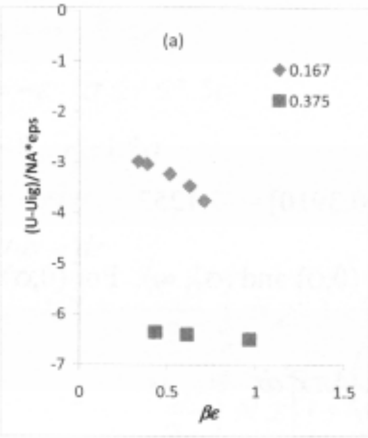
at $b\rho$=0.6*π/6=π/10 and $\beta\varepsilon$=1, $(U\text{-}Uig)/RT = -1.267$

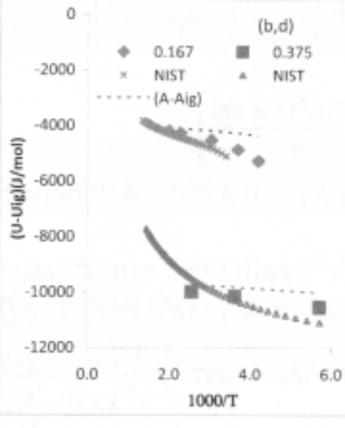
These expressions for energy departures are different because the rdf approximation is inexact. If rdf exact, E-eqn and P-eqn would give same result. The E-eqn is more accurate because it integrates the potential instead of differentiating imprecise P-values.

(8.37) Molecular simulation can be used to explore the accuracy…

Molecular simulation can be used to explore the accuracy and significance of individual contributions to an equation of state. Use the DMD module atEtomica.org to explore Xe's energy departure. (a) Plot $U/NA\varepsilon$ versus $\beta\varepsilon$ $\lambda = 1.7$ for $\eta_P = 0.167$ and 0.375 (b) using ε and σ from HW7.25, plot Xe's $U - U^{ig}$ versus $1000/T$ and showing the isochoric data for Xe from Webbook.nist.gov at 22.14 mol/L on the same axes. (c) The data for U – Uig exhibit a linear trend with $\beta\varepsilon$. The data for Z also exhibit a linear trend with βε. What trends do these two data sets indicate for $(A - A^{ig})_{TV}$/RT? Are they consistent? (d) Use the trapezoidal rule and the energy equation (Eqn. 7.49) to estimate A – Aig and plot as a dashed line. How accurate are your estimates (AAD%) and how could you improve them?

Solution:





(c) For SW fluid:Z = Z0 + Z1/T + Z2/T; (U-Uig)/RT = U1/T + U2/T Linear Z means Z2≈0, but non-zero slope of (U-U^{ig}) means U2≠0. So these are NOT exactly consistent. Since Z2 = ρdA2/dρ, it means A2~const. for this density range. If you look closely at Z vs. 1/T for η=0.167, it curves more.

(d) Extrapolating to T=∞ gives U-Uig= -9451.

(A-Aig)/RT = ∫(U-Uig)d(1/RT)

(8.38) Suppose two molecules had similar potential functions…

Suppose two molecules had similar potential functions, but they were mirror images of one another as shown in the figure below. Would A or B have the larger internal energy departure?

(a) Reason qualitatively but refer to appropriate equations to explain your answer.

(b) Compute the values of (U – Uig)/RT at a packing fraction of 0.4 and a temperature of 50

Solution: (U-Uig) = (ρ/2) ∫ u g 4π r^2 dr

(a) Qualitatively, it is a tough call because *g* is large when r is small, so the effects tend to cancel. For a guess, we could say that g decreases quickly to nearly 1.0, then the dominant effect should be the larger diameter. The larger diameter favors more energy at larger r to give the most energy, so this leads us to guess in favor of B.

(b) For a comparison, we can omit the factor of ρ/2. Integrating gives,

r(nm)	0.3	0.45	0.45	0.6
g(r)	6.93	0.91	0.91	1.05
r^2	0.09	0.2025	0.2025	0.36
uA	-100	-100	-50	-50
IntegrandA	-62.37	-18.43	-9.21	-18.90
uB	-50	-50	-100	-100
IntegrandB	-31.19	-9.21	-18.43	-37.80

IntegralA = (-62.37-18.43-9.21-18.90)/2 = -684.3

IntegralB = (-31.19-9.21-18.43-37.80)/2 = -604.5

So, in this case, it seems that the large value of *g* overwhelmed other effects, but it was a very large value. At lower densities, where *g* is not so spiky, the *r*^{2} effect would clearly dominate.