Quiz 9
Chemical Engineering Thermodynamics
March 17, 2016

9.6. Calculate the fugacity of ethane at 320 K and 70 bar using:

a. Generalized charts

b. The Peng-Robinson equation

-Indicate the state of ethane (vapor, liquid, solid) under these conditions.
-For part a, ***include the chart*** with your answer sheet showing determination of values.
-For part b, use the Peng-Robinson function given below (use constants to three sig. figs.).

9.10. Estimate the fugacity of pure *n*-pentane (C_5H_{12}) at 97°C and 7 bar by utilizing the virial equation.

-Indicate the state of n-pentane (vapor, liquid, solid) under these conditions.
-Ensure that the conditions of applicability for the virial equation are appropriate.
-Use the short-cut method.
-Also use the Antoine equation and compare the results.

$$\ln \varphi = \frac{P_r}{T_r}(B^0 + \omega B^1)$$

$Z = 1 + (B^0 + \omega B^1)P_r/T_r \quad \text{or} \quad Z = 1 + BP/RT$	7.6
where $B(T) = (B^0 + \omega B^1)RT_c/P_c$	7.7
$B^0 = 0.083 - 0.422/T_r^{1.6}$	7.8
$B^1 = 0.139 - 0.172/T_r^{4.2}$	7.9
Subject to $T_r > 0.686 + 0.439P_r$ or $V_r > 2.0$	7.10

$$\log_{10} P_r^{sat} = \frac{7}{3}(1+\omega)\left(1-\frac{1}{T_r}\right) \qquad 9.11$$

❗ Shortcut vapor pressure equation. Use care with the shortcut equation below $T_r = 0.5$.

$$\frac{(G-G^{ig})}{RT} = \ln\left(\frac{f}{P}\right) = \ln\varphi \qquad 9.22$$

$$\ln\varphi = -\ln(Z-B) - \frac{A}{B\sqrt{8}}\ln\left[\frac{Z+(1+\sqrt{2})B}{Z+(1-\sqrt{2})B}\right] + Z - 1 \qquad 9.33$$

$$A \equiv aP/R^2T^2 \qquad 7.21$$

$$B \equiv bP/RT \qquad 7.22$$

$$a \equiv a_c\alpha; \quad a_c \equiv 0.45723553\frac{R^2T_c^2}{P_c} \qquad b \equiv 0.07779607R\frac{T_c}{P_c} \qquad 7.16$$

$$\alpha \equiv [1+\kappa(1-\sqrt{T_r})]^2 \qquad \kappa \equiv 0.37464 + 1.54226\omega - 0.26992\omega^2 \qquad 7.17$$

$$Z^3 - (1-B)Z^2 + (A - 3B^2 - 2B)Z - (AB - B^2 - B^3) = 0 \qquad 7.25$$

❗ Poynting correction.

The fugacity is then calculated by

$$f = \varphi^{sat} P^{sat} \exp\left(\frac{V^L(P-P^{sat})}{RT}\right) \qquad 9.39$$

Saturated liquid volume can be estimated within a slight percent error using the **Rackett** equation

$$V^{satL} = V_c Z_c^{(1-T_r)^{0.2857}} \qquad 9.40$$

$$Z_c = P_c V_c/(RT_c)$$

$$f^L \approx \varphi^{sat} P^{sat} \quad \text{or commonly} \quad f^L \approx P^{sat} \qquad 9.41$$

Properties of Selected Compounds

*Heat capacities are values for **ideal gas at 298 K** and should be used for **order of magnitude calculations** only. See appendices for temperature-dependent formulas and constants.*

ID	Compound	T_c (K)	P_c (MPa)	ω	ρ g/cm^3	MW	C_P^{ig}/R	δ (J/cm^3)^{½}	α (J/cm^3)^{½}	β (J/cm^3)^{½}
Aliphatics										
1	METHANE	190.6	4.604	0.011	*0.29*	16	4.30	11.7	0	0
2	ETHANE	305.4	4.880	0.099	*0.43*	30	6.31	13.5	0	0
3	PROPANE	369.8	4.249	0.152	*0.58*	44	8.85	13.1	0	0
4	*n*-BUTANE	425.2	3.797	0.193	*0.60*	58	11.89	13.5	0	0
5	ISOBUTANE	408.1	3.648	0.177	*0.55*	58	11.70	12.5	0	0
7	*n*-PENTANE	469.7	3.369	0.249	0.62	72	14.45	14.3	0	0
8	ISOPENTANE	460.4	3.381	0.228	0.62	72	14.28	13.9	0	0
9	NEOPENTANE	433.8	3.199	0.196	0.60	72	14.62	13.1	0	0
11	*n*-HEXANE	507.4	3.012	0.305	0.66	86	17.21	14.9	0	0
17	*n*-HEPTANE	540.3	2.736	0.349	0.68	100	19.95	15.3	0	0
27	*n*-OCTANE	568.8	2.486	0.396	0.70	114	22.70	15.5	0	0
27	ISOOCTANE	544.0	2.570	0.303	0.70	114	22.50	14.1	0	0
46	*n*-NONANE	595.7	2.306	0.437	0.71	128	25.45	15.6	0	0
56	*n*-DECANE	618.5	2.123	0.484	0.73	142	28.22	15.7	0	0
64	*n*-DODECANE	658.2	1.824	0.575	0.75	170	33.71	15.9	0	0
66	*n*-TETRADECANE	696.9	1.438	0.570	0.76	198	39.22	16.1	0	0
68	*n*-HEXADECANE	720.6	1.419	0.747	0.77	226	44.54	16.2	0	0

Gas Constant, R

$= 8.31447$ J/mole-K $= 8.31447$ cm^3-MPa/mole-K $= 8.31447$ m^3-Pa/mole-K

$= 8{,}314.47$ cm^3-kPa/mole-K $= 83.1447$ cm^3-bar/mole-K $= 1.9859$ Btu/lbmole-R[see note 1]

$= 82.057$ cm^3-atm/mole-K $= 1.9872$ cal/mole-K[see note 2] $= 10.731$ ft^3-psia/lbmole-R

(Function values at 100 kPa and 288 K or the normal boiling temperature if greater.)

Substance	Formula	Molar mass M kg/mol	Boiling temp. T_b K	Critical temp T_{cr} K	Critical pressure p_{cr} MPa	Critical compressibility factor[a] Z_{cr}	Pitzer's acentric factor ω	Thermal capacity[b] c_p J/(kg·K)	Thermal conductivity[c] k W/(m·K)	Dynamic viscosity[d] $\mu \cdot 10^6$ Pa·s
n-Pentane	C_5H_{12}	0.072	309.2	470	3.38	0.262	0.251	1680	0.015	11.7
Phenol	C_6H_6O	0.094	455	694	6.13	0.243	0.426			
Propane	C_3H_8	0.044	231.1	370	4.26	0.281	0.152	1570	0.015	7.4
iso-Propanol	C_3H_8O	0.060	355.4	508	4.76	0.248	0.669	1540		
Propylene (propene)	C_3H_6	0.042	225.4	365	4.62	0.275	0.148	1460	0.014	8.1
Propylene glycol	$C_3H_8O_2$	0.076	461.3	626	6.10	0.280	1.107			

E.3. Antoine Constants

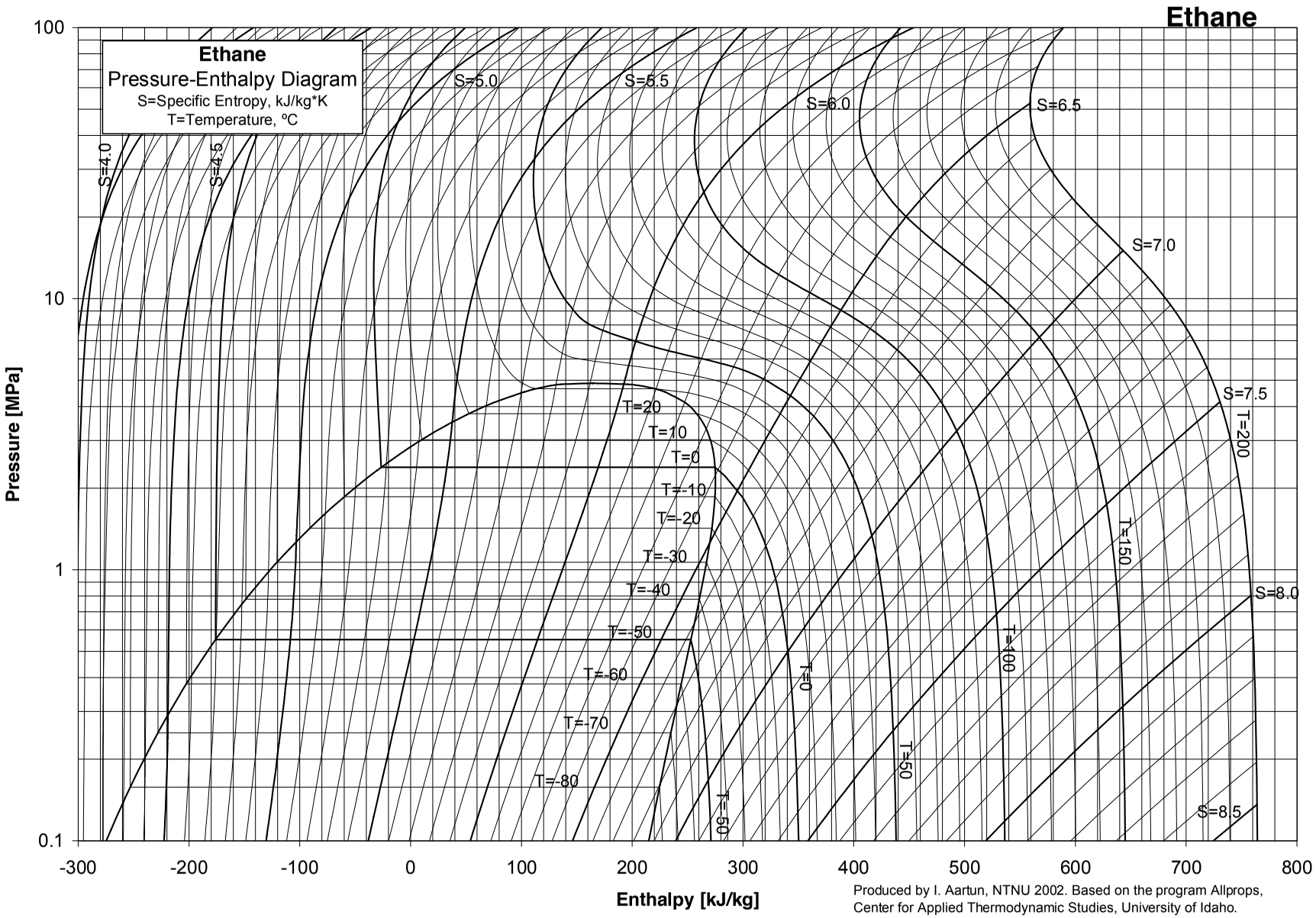
The following constants are for the equation

$$\log_{10} P^{sat} = A - \frac{B}{T + C}$$

where P^{sat} is in mmHg, and T is in Celsius. Additional Antoine constants are tabulated in

	A	B	C	T range (°C)	Source
Acetic acid	8.02100	1936.01	258.451	18–118	[a]
Acetic acid	8.26735	2258.22	300.97	118–227	[a]
Acetone	7.63130	1566.69	273.419	57–205	[a]
Acetone	7.11714	1210.595	229.664	−13–55	[a]
Acrolein (2-propenal)	8.62876	2158.49	323.36	2.5–52	[b]
Benzene	6.87987	1196.76	219.161	8–80	[a]
Benzyl chloride	7.59716	1961.47	236.511	22–180	[b]
Biphenyl (solid)	13.5354	4993.37	296.072	20–40	[c]
1-Butanol	7.81028	1522.56	191.95	30–70	[d]
1-Butanol	7.75328	1506.07	191.593	70–120	[d]
2-Butanone	7.28066	1434.201	246.499	−6.5–80	[b]
Chloroform	6.95465	1170.966	226.232	−10–60	[a]
Ethanol	8.11220	1592.864	226.184	20–93	[a]
Hexane	6.91058	1189.64	226.28	−30–170	[a]
1-Propanol	8.37895	1788.02	227.438	−15–98	[a]
2-Propanol	8.87829	2010.33	252.636	−26–83	[a]
Methanol	8.08097	1582.271	239.726	15–84	[a]
Naphthalene (solid)	8.62233	2165.72	198.284	20–40	[e]
Pentane	6.87632	1075.78	233.205	−50–58	[a]
3-Pentanone	7.23064	1477.021	237.517	36–102	[a]
Toluene	6.95087	1342.31	219.187	−27–111	[a]
Water	8.07131	1730.63	233.426	1–100	[a]

a. Gmehling, J., 1977-. *Vapor-liquid Equilibrium Data Collection*, Frankfort, Germany: DECHEMA.
b. Fit to data from Stull, D.R. in *Perry's Chemical Engineering Handbook*, 5th ed., McGraw-Hill, pp. 3-46 to 3-62.
c. Timmermans, J., 1950. *Physio-Chemical Constants of Pure Organic Compounds*, New York: Elsevier.
d. Fit to data from *Handbook of Chemistry and Physics*, 56th ed, R.C. Weast, ed., CRC Press, 1974–75, pp. D191–D210.
e. Fit to data of Ambrose, D., Lawerenson, I.J., Sprake, C.H.S. 1975. *J. Chem. Therm.* 7:1173.


Ethane
Ethane
Pressure-Enthalpy Diagram
S=Specific Entropy, kJ/kg*K
T=Temperature, ºC
Pressure [MPa]
Enthalpy [kJ/kg]
100
10
1
0.1
-300
-200
-100
0
100
200
300
400
500
600
700
800
S=4.0
S=4.5
S=5.0
S=5.5
S=6.0
S=6.5
S=7.0
S=7.5
S=8.0
S=8.5
T=20
T=10
T=0
T=-10
T=-20
T=-30
T=-40
T=-50
T=-60
T=-70
T=-80
T=-50
T=0
T=50
T=100
T=150
T=200
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Center for Applied Thermodynamic Studies, University of Idaho.

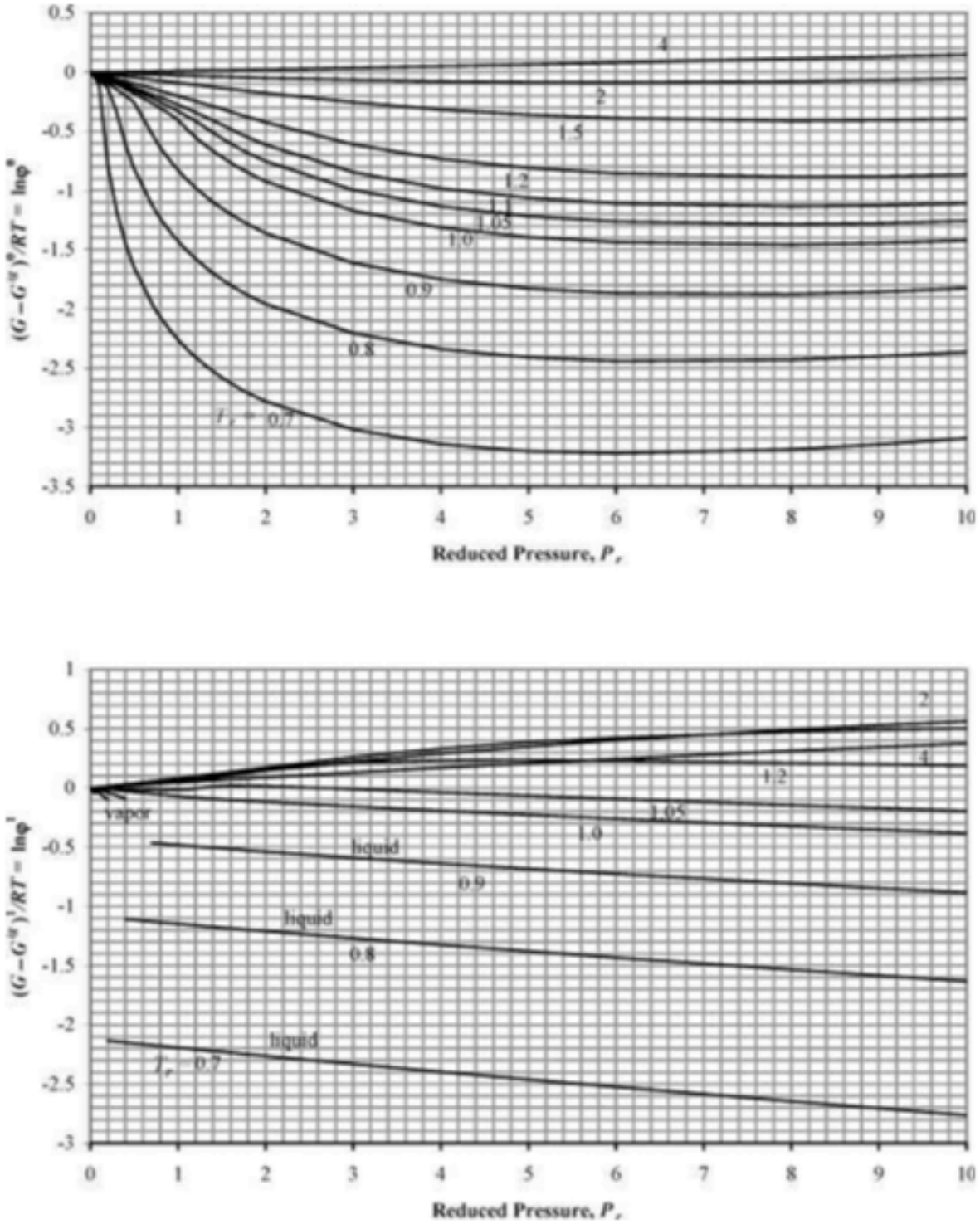

Figure 9.4. Generalized charts for estimating the Gibbs departure function using the Lee-Kesler equation of state. $(G - G^{ig})^0/RT$ uses $\omega = 0.0$, and $(G - G^{ig})^1/RT$ is the correction factor for a hypothetical compound with $\omega = 1.0$.

ANSWERS: **Quiz 9**
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9.6

(9.06) Calculate the fugacity of ethane at 320 K and 70 bar

a) Generalized chart
ethane: T_C =305.4 K, P_C =48.8 bar, ω=0.099

$$T_r = \frac{T}{T_C} = 320 / 305.4 = 1.048$$

$$P_r = \frac{P}{P_C} = 70 / 48.8 = 1.434$$

From charts, $\ln(\varphi^0) = -0.52$, $\ln(\varphi^1) = 0.01$
$\ln \varphi = \ln(\varphi^0) + \omega \ln(\varphi^1) = -0.52 + 0.099(0.01) = -0.52 \Rightarrow \varphi = 0.59$

$$f = \phi P = (0.59)(70) = 41.3 \text{ bar}$$

b) Can use PREOS.xls and read f, can use PRFUG.xls, or can use PRMIX.xls:
$\phi = 0.56909$
$f = 3.98366$ MPa = 39.84 bar

(9.10) Estimate the fugacity of pure n-pentane…

From the Antoine equation at 97 C, the vapor pressure is 4135 mmHg/750 = 5.5 bar = 0.55 MPa

Therefore, the fugacity will be given by

$f = f^{sat} \exp(V^L(P - P^{sat})/RT) = \varphi^{sat} P^{sat} \exp(V^L(P - P^{sat})/RT)$

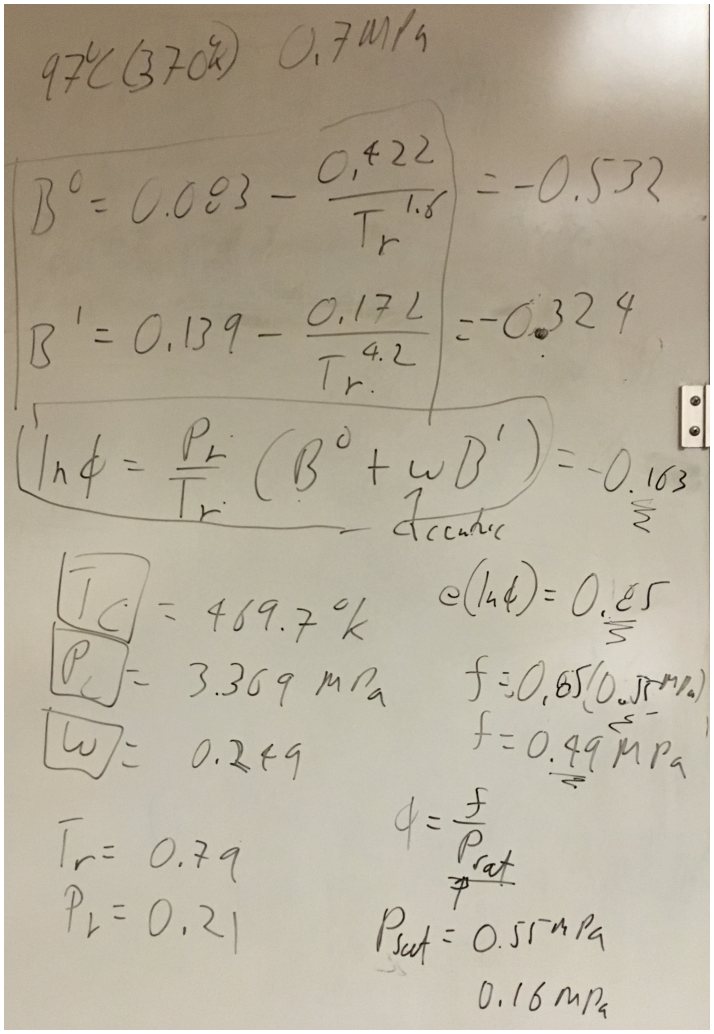
$\varphi^{sat} = \exp(BP^{sat}/RT)$

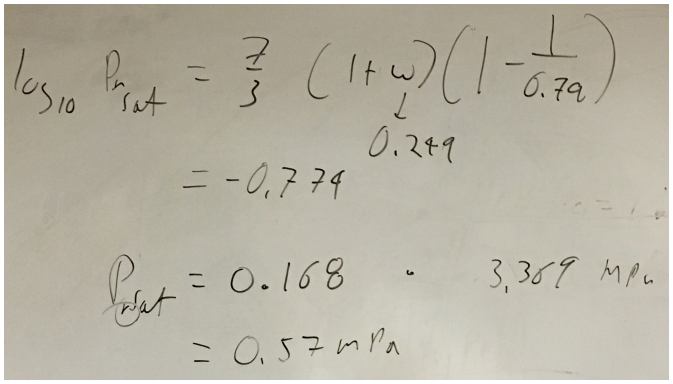
The virial equation can be calculated using Eqn. 6.9-6.10 at 370.15 K

B^0	B^1	BP_c/RT_c	$B(cm^3/mol)$
-0.535	-0.329	-0.617	-714.73

$\varphi^{sat} = \exp(-714.73*0.55/8.314/370.15) = 0.880 \Rightarrow f^{sat} = 0.55*0.88 = 0.484$ MPa

V^L from Rackett correlation (Eqn. 8.37) = $V_c Z_c^{(1-Tr)^{0.2857}} = 311.8(0.269)^{(1-0.788)^{0.2857}} = 134$ cm^3/mol
$f = 0.484*\exp(134(0.7 - 0.55)/8.314/370.15) = 0.487$ MPa


97°C (370K) 0.7 MPa
$B^0 = 0.083 - \frac{0.422}{T_r^{1.6}} = -0.532$
$B^1 = 0.139 - \frac{0.172}{T_r^{4.2}} = -0.324$
$\ln\phi = \frac{P_r}{T_r}(B^0 + \omega B^1) = -0.163$
accurate
$T_c = 469.7\ K$
$P_c = 3.369\ MPa$
$\omega = 0.249$
$T_r = 0.79$
$P_r = 0.21$
$\sigma(\ln\phi) = 0.05$
$f = 0.65(0.55\ MPa)$
$f = 0.49\ MPa$
$\phi = \frac{f}{P_{sat}}$
$P_{sat} = 0.55\ MPa$
$0.16\ MPa$


$\log_{10} P_{r sat} = \frac{7}{3}(1+\omega)\left(1 - \frac{1}{0.79}\right)$
$\omega = 0.249$
$= -0.774$
$P_{r sat} = 0.168$ · $3.369\ MPa$
$= 0.57\ MPa$