PETE 310
Lectures # 34 to 35

Cubic Equations of State

...Last Lectures

Instructional Objectives

- Know the data needed in the EOS to evaluate fluid properties
- Know how to use the EOS for single and for multicomponent systems
- Evaluate the volume (density, or z-factor) roots from a cubic equation of state for
  - Gas phase (when two phases exist)
  - Liquid Phase (when two phases exist)
  - Single phase when only one phase exists

Equations of State (EOS)

- Single Component Systems

  Equations of State (EOS) are mathematical relations between pressure (P) temperature (T), and molar volume (V).
- Multicomponent Systems

  For multicomponent mixtures in addition to (P, T & V) , the overall molar composition and a set of mixing rules are needed.

Uses of Equations of State (EOS)

- Evaluation of gas injection processes (miscible and immiscible)
- Evaluation of properties of a reservoir oil (liquid) coexisting with a gas cap (gas)
- Simulation of volatile and gas condensate production through constant volume depletion evaluations
- Recombination tests using separator oil and gas streams
- Many more…

Equations of State (EOS)

- One of the most used EOS' is the Peng-Robinson EOS (1975). This is a three-parameter corresponding states model.

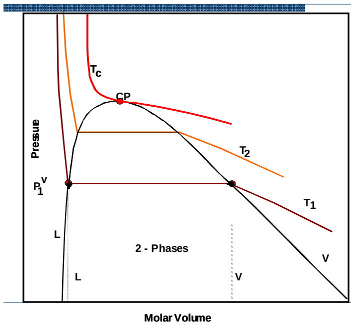
$$P = \frac{RT}{V-b} - \frac{a\alpha}{V(V+b)+b(V-b)}$$

$$P = P_{rep} + P_{attr}$$

Equations of State (EOS)

- Peng-Robinson EOS is a three-parameter corresponding states model.
  - Critical Temperature T_c
  - Critical Pressure P_c
  - Acentric factor ω

PV Phase Behavior



Pressure-volume behavior indicating isotherms for a pure component system

Equations of State (EOS)

- The critical point conditions are used to determine the EOS parameters

$$\left(\frac{\partial P}{\partial V}\right)_{T_c} = 0$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_{T_c} = 0$$

Equations of State (EOS)

- Solving these two equations simultaneously for the Peng-Robinson EOS provides

$$a = \Omega_a \frac{R^2 T_c^2}{P_c} \quad \textbf{and} \quad b = \Omega_b \frac{R T_c}{P_c}$$

Equations of State (EOS)

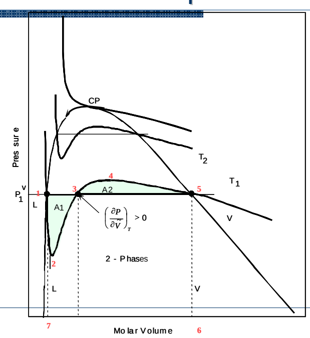
Where $\Omega_a = 0.45724$

and $\Omega_b = 0.07780$

with $\alpha = \left(1 + m\left(1 - \sqrt{T_r}\right)\right)^2$

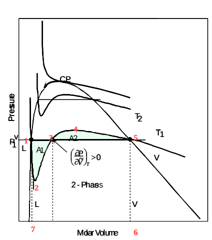
$$m = 0.37464 + 1.54226\omega - 0.2699\omega^2$$

EOS for a Pure Component



EOS for a Pure Component

- Maxwell equal area rule (Van der Waals loops)
- For a fixed Temperature lower than T_c the vapor pressure is found when $A_1 = A_2$
- Equations of State <u>cannot</u> be quadratic polynomials
- Lowest root is liquid molar volume, largest root is gas molar volume
- Middle root has no physical significance



Equations of State (EOS)

- Phase equilibrium for a single component at a given temperature can be graphically determined by selecting the saturation pressure such that the areas above and below the loop are equal, these are known as the van der Waals loops.

Equations of State (EOS)

- PR equation can be expressed as a cubic polynomial in V, density, or Z.

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

with $A = \dfrac{a\alpha P}{(RT)^2}$, $B = \dfrac{bP}{RT}$

Equations of State (EOS)

- When working with mixtures (aα) and (b) are evaluated using a set of mixing rules
- The most common mixing rules are:
  - Quadratic for a
  - Linear for b

Quadratic MR for *a*

$$(a\alpha)_m = \sum_{i=1}^{Nc}\sum_{j=1}^{Nc} x_i x_j \left(a_i a_j \alpha_i \alpha_j\right)^{0.5} \left(1-k_{ij}\right)$$

- where k_{ij}'s are the binary interaction parameters and by definition

$$k_{ij} = k_{ji}$$

$$k_{ii} = 0$$

Linear MR for b

$$b_m = \sum_{i=1}^{Nc} x_i b_i$$

Example

- For a three-component mixture (Nc = 3) the attraction (a) and the repulsion constant (b) are given by

$$(a\alpha)_m = 2x_1x_2\left(a_1a_2\alpha_1\alpha_2\right)^{0.5}(1-k_{12}) + 2x_2x_3\left(a_2a_3\alpha_2\alpha_3\right)^{0.5}(1-k_{23}) + 2x_1x_3\left(a_1a_3\alpha_1\alpha_3\right)^{0.5}(1-k_{13}) + x_1^2\left(a_1\alpha_1\right) + x_2^2\left(a_2\alpha_2\right) + x_3^2\left(a_3\alpha_3\right)$$

$$b_m = x_1b_1 + x_2b_2 + x_3b_3$$

Equations of State (EOS)

- The constants a and b are evaluated using
  - Overall compositions z_i with $i = 1, 2 \ldots Nc$
  - Liquid compositions x_i with $i = 1, 2 \ldots Nc$
  - Vapor compositions y_i with $i = 1, 2 \ldots Nc$

Equations of State (EOS)

- The cubic expression for a mixture is then evaluated using

$$A_m = \frac{(a\alpha)_m P}{(RT)^2} \qquad B_m = \frac{b_m P}{RT}$$

Analytical Solution of Cubic Equations

- The cubic EOS can be arranged into a polynomial and be solved analytically as follows.

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

Analytical Solution of Cubic Equations

- Let's write the polynomial in the following way

$$x^3 + a_1 x^2 + a_2 x + a_3 = 0$$

Note: "x" could be either the molar volume, or the density, or the z-factor

Analytical Solution of Cubic Equations

- When the equation is expressed in terms of the z factor, the coefficients a_1 to a_3 are:

$$a_1 = (B - 1)$$

$$a_2 = (A - 3B^2 - 2B)$$

$$a_3 = -(AB - B^2 - B^3)$$

Procedure to Evaluate the Roots of a Cubic Equation Analytically

- Let

$$Q = \frac{3a_2 - a_1^2}{9}$$

$$R = \frac{9a_1 a_2 - 27a_3 - 2a_1^3}{54}$$

$$S = \sqrt[3]{R + \sqrt{Q^3 + R^2}}$$

$$T = \sqrt[3]{R - \sqrt{Q^3 + R^2}}$$

Procedure to Evaluate the Roots of a Cubic Equation Analytically

- The solutions are,

$$x_1 = S + T - \frac{1}{3}a_1$$

$$x_2 = -\frac{1}{2}(S+T) - \frac{1}{3}a_1 + \frac{1}{2}i\sqrt{3}(S-T)$$

$$x_3 = -\frac{1}{2}(S+T) - \frac{1}{3}a_1 - \frac{1}{2}i\sqrt{3}(S-T)$$

Procedure to Evaluate the Roots of a Cubic Equation Analytically

- If a_1, a_2 and a_3 are real (always here) The discriminant is

  $D = Q^3 + R^2$

  Then
  - One root is real and two complex conjugate if $D > 0$;
  - All roots are real and at least two are equal if $D = 0$;
  - All roots are real and unequal if $D < 0$.

Procedure to Evaluate the Roots of a Cubic Equation Analytically

$$\text{If } D < 0 \Rightarrow \begin{cases} x_1 = 2\sqrt{-Q}\cos\left(\frac{1}{3}\theta\right) - \frac{1}{3}a_1 \\ x_2 = 2\sqrt{-Q}\cos\left(\frac{1}{3}\theta + 120^\circ\right) - \frac{1}{3}a_1 \\ x_3 = 2\sqrt{-Q}\cos\left(\frac{1}{3}\theta + 240^\circ\right) - \frac{1}{3}a_1 \end{cases}$$

where

$$\cos\theta = \frac{R}{\sqrt{-Q^3}}$$

Procedure to Evaluate the Roots of a Cubic Equation Analytically

$$x_1 + x_2 + x_3 = -a_1$$

$$x_1 x_2 + x_2 x_3 + x_3 x_1 = a_2$$

$$x_1 x_2 x_3 = -a_3$$

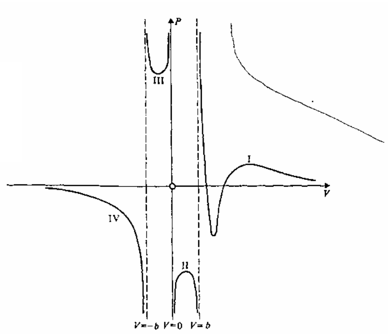
where x_1, x_2 and x_3 are the three roots.

Procedure to Evaluate the Roots of a Cubic Equation Analytically

- The range of solutions useful for engineers are those for positive volumes and pressures, we are not concerned about imaginary numbers.

Solutions of a Cubic Polynomial

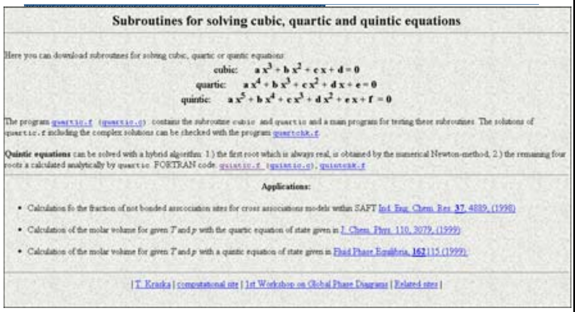
We are only interested in the first quadrant.



Solutions of a Cubic Polynomial

- http://www.uni-koeln.de/math-nat-fak/phchem/deiters/quartic/quartic.html contains Fortran codes to solve the roots of polynomials up to fifth degree.

Web site to download Fortran source codes to solve polynomials up to fifth degree



Subroutines for solving cubic, quartic and quintic equations

Here you can download subroutines for solving cubic, quartic or quintic equations:

cubic: $a x^3 + b x^2 + c x + d = 0$

quartic: $a x^4 + b x^3 + c x^2 + d x + e = 0$

quintic: $a x^5 + b x^4 + c x^3 + d x^2 + e x + f = 0$

The program quartic.f (quartic.c) contains the subroutine cubic and quartic and a main program for testing these subroutines. The solutions of quartic.f including the complex solutions can be checked with the program quartchk.f.

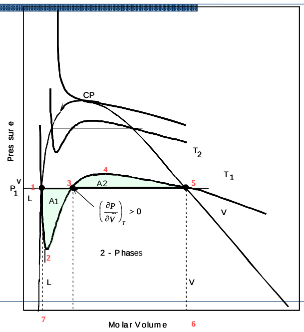
Quintic equations can be solved with a hybrid algorithm: 1.) the first root which is always real, is obtained by the numerical Newton-method, 2.) the remaining four roots a calculated analytically by quartic FORTRAN code: quintic.f (quintic.c), quintchk.f

Applications:

- Calculation fo the fraction of not bonded association sites for cross associations models within SAFT Ind. Eng. Chem. Res. **37**, 4889, (1998)
- Calculation of the molar volume for given *T* and *p* with the quartic equation of state given in J. Chem. Phys. 110, 3079, (1999)
- Calculation of the molar volume for given *T* and *p* with a quintic equation of state given in Fluid Phase Equilibria, **162** 115 (1999)

| T. Kraska | computational site | 1st Workshop on Global Phase Diagrams | Related sites |

EOS for a Pure Component



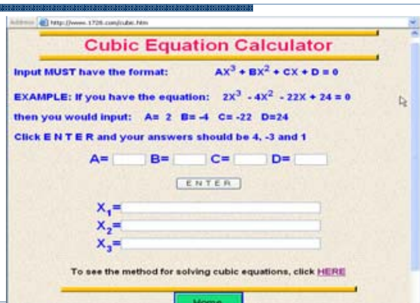
Parameters needed to solve EOS

- Tc, Pc, (acentric factor for some equations i.e. Peng Robinson)
- Compositions (when dealing with mixtures)
- For a single component
  - Specify P and T → determine Vm
  - Specify P and Vm → determine T
  - Specify T and Vm → determine P

Tartaglia: the solver of cubic equations

http://es.rice.edu/ES/humsoc/Galileo/Catalog/Files/tartalia.html

Cubic Equation Solver



http://www.1728.com/cubic.htm

WWW Cubic Equation Solver

- Only to check your results
- You will not be able to use it in the exam if needed
- Special bonus HW will be invalid if using this code, you MUST provide evidence of work
- Write your own code (Excel is OK)

Two-phase VLE

- The phase equilibria equations are expressed in terms of the equilibrium ratios, the "K-values".

$$K_i = \frac{y_i}{x_i} = \frac{\hat{\phi}_i^l}{\hat{\phi}_i^v}$$

Dew Point Calculations

- Equilibrium is always stated as:

$$x_i \hat{\phi}_i^l P = y_i \hat{\phi}_i^v P \quad \text{(i = 1, 2, 3 ,...Nc)}$$

- with the following material balance constrains

$$\sum_{i=1}^{Nc} x_i = 1, \qquad \sum_{i=1}^{Nc} y_i = 1, \qquad \sum_{i=1}^{Nc} z_i = 1$$

Dew Point Calculations

- At the dew-point

$$x_i\hat{\phi}_i^l = z_i\hat{\phi}_i^v$$

$$x_i K_i = z_i \qquad (i = 1, 2, 3, \ldots Nc)$$

Dew Point Calculations

- Rearranging, we obtain the Dew-Point objective function

$$\sum_{i=1}^{Nc} \frac{z_i}{K_i} - 1 = 0$$

Bubble Point Equilibrium Calculations

- For a Bubble-point

$$\sum_{i=1}^{Nc} z_i K_i - 1 = 0$$

Flash Equilibrium Calculations

- Flash calculations are the work-horse of any compositional reservoir simulation package.
- The objective is to find the f_v in a VL mixture at a specified T and P such that

$$\sum_{i=1}^{N_c} \frac{z_i(K_i-1)}{1+f_v(K_i-1)} = 0$$

Evaluation of Fugacity Coefficients and K-values from an EOS

- The general expression to evaluate the fugacity coefficient for component "*i*" is

$$\left\{ RT \ln \hat{\phi}_i^v = \int_0^P \left[\bar{V}_i - \frac{RT}{P} \right] dP \right\}_{T=fixed}$$

Evaluation of Fugacity Coefficients and K-values from an EOS

- The final expression to evaluate the fugacity coefficient of component *'i'* in the vapor phase using an EOS is.

$$RT \ln \hat{\phi}_i^v = -\int_{\infty}^{V_t^v} \left[\left(\frac{\partial P}{\partial n_i^v} \right)_{T, n_j^v \neq i} - \frac{RT}{V_t^v} \right] dV_t^v - RT \ln Z_v$$

- A similar expression replacing *v* by *l* is used for the liquid

Equations of State are not perfect…

- EOS provide self consistent fluid properties
  - Density (o & g) trends are correctly predicted with pressure, temperature, and compositions (and all derived properties…)
  - Same phase equilibrium model for gas and liquid phases (material balance consistency)

Equations of State are not perfect…

- However… predicted fluid property values may differ substantially from data
- EOS are routinely "calibrated" to selected & limited experimental data
- After "calibration" EOS predictions beyond range of data can be used with confidence
- EOS are extensively used in reservoir simulation

What is EOS calibration?

- Minimization of squared differences between experimental and predicted fluid properties

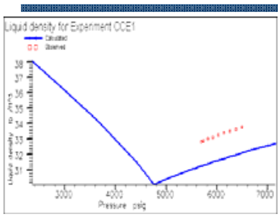
$$\sum_{i=1}^{Ndata} \left(g_i^{predicted} - g_i^{experimental} \right)^2 = min$$

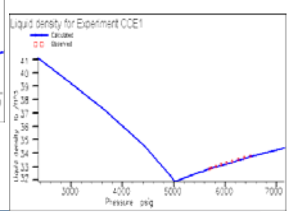
- These Properties (g_i) include:
  - Densities, saturation pressures
  - Relative amounts of gas and liquid phases
  - Compositions, etc.

What is EOS calibration?

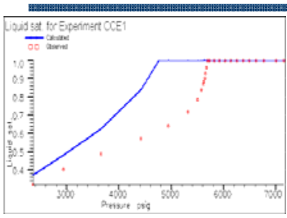
- Accomplished by changing within certain limits <u>selected</u> EOS parameters
- Minor adjustments (1 to 2%) of binary interaction parameters (k_{ij}) can change saturation pressures by 20 to 30%
- Different properties of the C_7^+ fraction affect liquid dropout and densities. These properties include
  - Molecular weight (uncertainty is +/- 10%)
  - Specific gravity
  - Critical properties and acentric factors which are highly dependent on correlations – Cannot be easily measured and not usually done.

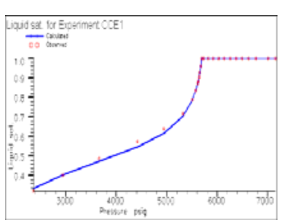
Pre and post calibration predictions from an EOS



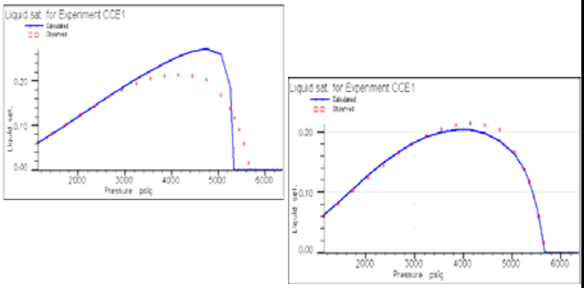


Pre and post calibration predictions from an EOS

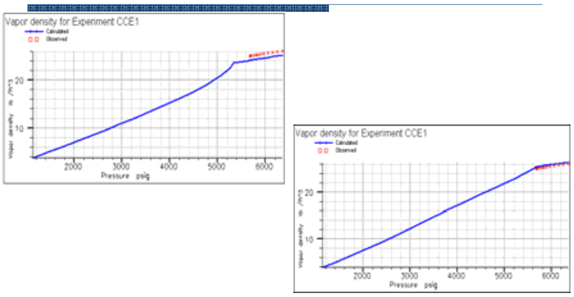




Pre and post calibration predictions from an EOS



Pre and post calibration predictions from an EOS



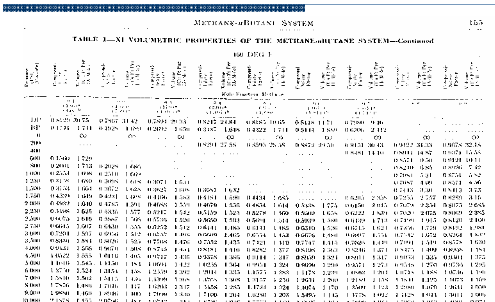
Special Homework Bonus

- Determine the equilibrium ratio of C_1 from multiple flash calculations using SOPE. Select <u>a mixture</u> and a suitable pressure temperature range
  - Discuss the trends, how does k_{C1} change with T at a fixed P?
  - Discuss the trends, how does k_{C1} change with P at a fixed T?
  - Provide well documented graphs

Special Homework Bonus

- Compare the equilibrium ratio of C_1 at 4000 psia and at 200 ºF with that of the convergence pressure chart using.
  - A mixture of C_1 and C_2
  - A mixture of C_1 and C_4
  - A mixture of C_1 and C_8
  - Discuss the results obtained and provide overlapped plots
- Calibrate one of EOS's in SOPE to the bubble point data reported by Standings in the following table

Special Homework Bonus



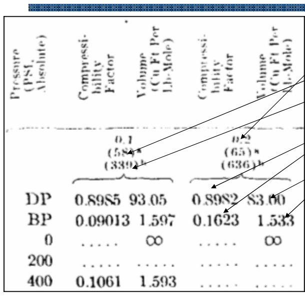
METHANE-*n*BUTANE SYSTEM 155

TABLE 1—XI VOLUMETRIC PROPERTIES OF THE METHANE-*n*BUTANE SYSTEM—Continued

160 DEG F

Pressure (PSI, Absolute)	Compressibility Factor (0.1)	Volume (Cu Ft Per Lb-Mole) (0.1)	Compressibility Factor (0.2)	Volume (Cu Ft Per Lb-Mole) (0.2)	Compressibility Factor (0.3)	Volume (Cu Ft Per Lb-Mole) (0.3)	Compressibility Factor (0.4)	Volume (Cu Ft Per Lb-Mole) (0.4)	Compressibility Factor (0.5)	Volume (Cu Ft Per Lb-Mole) (0.5)	Compressibility Factor (0.6)	Volume (Cu Ft Per Lb-Mole) (0.6)	Compressibility Factor (0.7)	Volume (Cu Ft Per Lb-Mole) (0.7)	Compressibility Factor (0.8)	Volume (Cu Ft Per Lb-Mole) (0.8)	Compressibility Factor (0.9)	Volume (Cu Ft Per Lb-Mole) (0.9)
DP	0.8129	30.75	0.7867	31.42	0.7894	29.33	0.8217	24.84	0.8185	19.65	0.8118	11.71	0.7980	9.46	.....	.....	.....	.....
BP	0.1711	1.741	0.1928	1.689	0.2892	1.650	0.3187	1.648	0.4322	1.711	0.5144	1.880	0.6206	2.412	.....	.....	.....	.....
0	.....	∞	.....	∞	.....	∞	.....	∞	.....	∞	.....	∞	.....	∞	.....	∞	.....	∞
200	.....	.....	.....	.....	.....	.....	0.8201	27.58	0.8595	28.58	0.8872	29.50	0.9151	30.43	0.9122	31.33	0.9078	32.18
400	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	0.8481	14.10	0.8914	14.87	0.9071	15.58
600	0.1569	1.729	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	0.8571	9.50	0.9121	10.11
800	0.2061	1.713	0.2028	1.686	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	0.8240	6.85	0.8926	7.42
1,000	0.2553	1.698	0.2510	1.669	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	0.7981	5.31	0.8754	5.82
1,250	0.3158	1.680	0.3098	1.648	0.3071	1.641	.....	.....	.....	.....	.....	.....	.....	.....	0.7687	4.09	0.8571	4.56
1,500	0.3753	1.664	0.3672	1.628	0.3627	1.608	0.3681	1.632	.....	.....	.....	.....	.....	.....	0.7413	3.30	0.8413	3.73
1,750	0.4339	1.649	0.4231	1.608	0.4166	1.583	0.4181	1.590	0.4434	1.685	.....	.....	0.6205	2.358	0.7255	2.757	0.8280	3.15
2,000	0.4932	1.640	0.4785	1.591	0.4688	1.559	0.4679	1.556	0.4854	1.614	0.5338	1.775	0.6150	2.045	0.7079	2.354	0.8075	2.685
2,250	0.5498	1.625	0.5335	1.577	0.5217	1.542	0.5159	1.525	0.5278	1.560	0.5609	1.658	0.6222	1.839	0.7020	2.075	0.8069	2.385
2,500	0.6075	1.616	0.5887	1.566	0.5736	1.526	0.5650	1.503	0.5691	1.514	0.5939	1.580	0.6439	1.713	0.7190	1.913	0.8120	2.160
2,750	0.6645	1.607	0.6430	1.555	0.6252	1.512	0.6141	1.485	0.6141	1.485	0.6340	1.536	0.6715	1.624	0.7356	1.779	0.8192	1.981
3,000	0.7201	1.597	0.6966	1.542	0.6757	1.498	0.6609	1.465	0.6554	1.453	0.6676	1.480	0.6997	1.551	0.7542	1.672	0.8264	1.832
3,500	0.8330	1.584	0.8026	1.525	0.7768	1.476	0.7552	1.435	0.7421	1.410	0.7747	1.415	0.7626	1.449	0.7991	1.519	0.8578	1.630
4,000	0.9431	1.568	0.9070	1.508	0.8745	1.454	0.8481	1.410	0.8282	1.377	0.8198	1.363	0.8246	1.371	0.8475	1.409	0.8958	1.484
4,500	1.0522	1.555	1.0116	1.495	0.9717	1.436	0.9378	1.386	0.9114	1.347	0.8959	1.324	0.8911	1.317	0.9033	1.335	0.9301	1.375
5,000	1.1616	1.545	1.1150	1.483	1.0691	1.422	1.0235	1.361	0.9951	1.324	0.9699	1.290	0.9571	1.273	0.9548	1.270	0.9736	1.295
6,000	1.3750	1.524	1.3154	1.458	1.2559	1.392	1.2044	1.335	1.1575	1.283	1.1178	1.239	1.0862	1.204	1.0718	1.188	1.0736	1.190
7,000	1.5840	1.502	1.5115	1.436	1.4399	1.368	1.3768	1.308	1.3157	1.250	1.2631	1.200	1.2189	1.158	1.1840	1.125	1.1673	1.109
8,000	1.7876	1.486	1.7016	1.417	1.6203	1.347	1.5458	1.285	1.4724	1.224	1.4074	1.170	1.3509	1.123	1.2980	1.079	1.2634	1.050
9,000	1.9880	1.469	1.8946	1.400	1.7999	1.330	1.7106	1.264	1.6280	1.203	1.5495	1.145	1.4778	1.092	1.4128	1.044	1.3614	1.006
10,000	2.1878	1.455	2.0796	1.384	1.9747	1.314	1.8736	1.246	1.7773	1.182	1.6886	1.123	1.5899	1.064	1.5232	1.013	1.4601	0.971

Special Homework Bonus



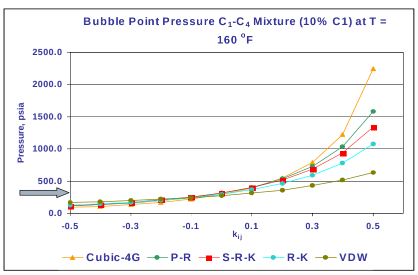
Pressure (PSI, Absolute)	Compressibility Factor	Volume (Cu Ft Per Lb-Mole)	Compressibility Factor	Volume (Cu Ft Per Lb-Mole)
	0.1 (584)[a] (339)[b]		0.2 (655)[a] (636)[b]	
DP	0.8985	93.05	0.8982	83.00
BP	0.09013	1.597	0.1623	1.533
0	.....	∞	.....	∞
200	.....	.....	.....	.....
400	0.1061	1.593	.....	.....

- Mole fraction of C1
- Dew point pressure
- Bubblepoint pressure
- Z-factors of mixture (gas and liquid)
- Molar volumes of mixture gas & liquid
  - All at T = 160ºF (not shown here)

Special Homework Bonus

- Select one EOS (Vdw, RK, SRK, PR, or Cubic-4G)
- Select one bubble point pressure for one composition of methane
- Plot pb predicted vs binary interaction parameter selected
- Select the best kij that matches the bubble point pressure
- Compare the values of experimental vs. predicted molar volumes

You should be obtaining a plot like this one...



Experimental p_b is 339 psia

You CANNOT use this same composition in Your homework

This is the end, we survived!!!