(P15.5)

(a) Perform bubble P calculations 1-CO2, 2- ethylene. For kij = 0

```
 COMPONENT IS  CARBON DIOXIDE         ID NO. IS   909
 COMPONENT IS  ETHYLENE               ID NO. IS   201
 T(K)= 222.00  P(MPa)= .8725        ZL= .2138E-01   ZV= .8674
  ID      LIQUID X   VAPOR Y    Yi/Xi
  909       .5000     .4057    .8114
  201       .5000     .5943    1.189
```

repeating across the composition range:

x1	y1	P(MPa)
0.0	0.0	1.02
0.1	0.0795	0.995
0.5	0.406	0.873
0.9	0.834	0.7012
1.	1.	0.642

End points were determined using bubble point pressure calculation using PRMIX for a single component. No azeotrope exists.

Answer is 0.87MPa

(b) Output from prmix.exe:

```
Kij MATRIX MODIFIED
              909     201
   201   .1100
```

```
bp
 COMPONENT IS  CARBON DIOXIDE         ID NO. IS   909
 COMPONENT IS  ETHYLENE               ID NO. IS   201
 T(K)= 222.00  P(MPa)= 1.126        ZL= .2867E-01   ZV= .8358
  ID      LIQUID X   VAPOR Y    Yi/Xi
  909       .5000     .4237    .8475
  201       .5000     .5763    1.153
```

For kij = 0.11

x1	y1	P(MPa)
0.0	0.0	1.02
0.1	0.139	1.09
0.5	0.424	1.126
0.9	0.691	0.882
1.	1.	0.642

at small x1, x1<y1. At large x1, x1>y1. Also, P maximum in mixture. Therefore, maximum P (minimum T) azeotrope will exist.

Answer is 11.3 bar.

(P15.6)
(a)
Pentane 7
Acetone 1051

```
THE DEFAULT Kij MATRIX IS
                7    1051
  1051   .0000

bp
 COMPONENT IS  n-PENTANE             ID NO. IS     7
 COMPONENT IS  ACETONE               ID NO. IS  1051
 T(K)= 305.05  P(MPa)= .7785E-01   ZL= .3247E-02   ZV= .9697
  ID      LIQUID X   VAPOR Y    Yi/Xi
    7       .7280     .8345    1.146
 1051       .2720     .1655    .6083

Answer: 0.78 bar, y1 = 0.83
```

(b) x=0.134 perform bubble pressure calcs adjusting kij until converge on experimental pressure of 1 bar at 0.728.

```
ki
  Kij =  0.11
 REQUIRED NUMBER OF ITERATIONS WAS:          7
 COMPONENT IS  n-PENTANE             ID NO. IS     7
 COMPONENT IS  ACETONE               ID NO. IS  1051
 T(K)= 305.05  P(MPa)= .9927E-01   ZL= .4199E-02   ZV= .9634
  ID      LIQUID X   VAPOR Y    Yi/Xi
    7       .7280     .7167    .9845
 1051       .2720     .2833    1.041

  Kij =  0.117
 REQUIRED NUMBER OF ITERATIONS WAS:          5
 COMPONENT IS  n-PENTANE             ID NO. IS     7
 COMPONENT IS  ACETONE               ID NO. IS  1051
 T(K)= 305.05  P(MPa)= .1011       ZL= .4282E-02   ZV= .9629
  ID      LIQUID X   VAPOR Y    Yi/Xi
    7       .7280     .7078    .9723
 1051       .2720     .2922    1.074
```

Intermediate Answer: k_{ij} = 0.117 to fit bubble pressure, azeotrope composition not matched exactly.

```
bp
 COMPONENT IS  n-PENTANE             ID NO. IS     7
 COMPONENT IS  ACETONE               ID NO. IS  1051
 T(K)= 312.75  P(MPa)= .1120       ZL= .3881E-02   ZV= .9626
  ID      LIQUID X   VAPOR Y    Yi/Xi
    7       .1340     .5453    4.070
 1051       .8660     .4547    .5250
```

Answer: k_{ij} = 0.117, BP = 1.12 bar

(P15.7)

a) using shortcut K-ratio equation at 298K, predict the vapor pressure of components.

#	COMPOUND	Psat (MPa)
1	CO2	6.44
2	METHANE	32.6
3	PROPANE	0.956
4	ETHANE	4.21

Note: methane is supercritical so the vapor pressure is extrapolated.
$y_iP = x_iP_i^{sat}$, $x_i = y_iP/P_i^{sat}$ → guess P until $\Sigma x_i = 1$.
$P_{NEW} = P_{OLD} / \Sigma$ xi

P(MPa)	X1	X2	X3	X4	Σ xi
3	0.14	0.028	0.628	0.143	0.939
3.19	0.149	0.029	0.667	0.152	0.997
3.2	0.15	0.0295	0667	0.153	0.9995

(b) there isn't a DP routing, use dt routine, guess P until DT = 298

```
REQUIRED NUMBER OF ITERATIONS WAS:           6
 COMPONENT IS  CARBON DIOXIDE         ID NO. IS   909
 COMPONENT IS  METHANE                ID NO. IS     1
 COMPONENT IS  PROPANE                ID NO. IS     3
 COMPONENT IS  ETHANE                 ID NO. IS     2
 T(K)= 286.67  P(MPa)= 3.000        ZL= .9407E-01   ZV= .7509
  ID      LIQUID X   VAPOR Y    Yi/Xi
  909       .2207     .3000    1.360
    1       .0715     .3000    4.198
    3       .5197     .2000    .3848
    2       .1882     .2000    1.063

T(K)= 295.61  P(MPa)= 4.000        ZL= .1286       ZV= .6876
  ID      LIQUID X   VAPOR Y    Yi/Xi
  909       .2410     .3000    1.245
    1       .0958     .3000    3.132
    3       .4637     .2000    .4313
    2       .1995     .2000    1.003
```

```
T(K)= 298.45  P(MPa)= 4.400       ZL= .1434       ZV= .6624
  ID      LIQUID X   VAPOR Y    Yi/Xi
  909       .2486      .3000    1.207
    1       .1064      .3000    2.819
    3       .4421      .2000    .4524
    2       .2029      .2000    .9856
```

P = 4.4MPA, DT = 298.5 close enough.

P(MPa)	x1	x2	x3	x4
4.4	0.249	0.107	0.442	0.203

PR predicts much different P and composition. PR should be improved by using non-zero kij from binary data fits for even more accuracy.

(P15.8) $Z = 1 + \dfrac{4cb\rho}{1-b\rho}$, Note we can integrate more easily using $\left[\dfrac{db\rho}{b\rho} = \dfrac{d\rho}{\rho}\right]$

$$\frac{(A-A^{ig})_{TV}}{RT} = 4\int_0^{b\rho} \frac{c}{(1-b\rho)}\, d(b\rho) = -4c\ln(1-b\rho) \quad \text{.....Eqn. 8.27}$$

$$\ln(\hat{\varphi}_i) = \frac{(\mu_i - \mu_i^{ig})}{RT} = \left[\frac{\partial (A-A^{ig})_{TV}/RT}{\partial n_i}\right]_{T,V,n_{j\neq i}} - \ln Z \quad \text{.....Eqn. 15.17}$$

$$\ln(\hat{\varphi}_i) = \left(\frac{\partial(-4nc*\ln(1-b\rho))}{\partial n_i}\right)_{T,\underline{V},n_{j\neq i}} - \ln Z$$

$$= -4\ln(1-b\rho)\left(\frac{\partial(nc)}{\partial n_i}\right)_{T,\underline{V},n_{j\neq i}} + 4nc\frac{1}{1-b\rho}\left(\frac{\partial(b\rho)}{\partial n_i}\right)_{T,\underline{V},n_{j\neq i}} - \ln Z$$

$$\left(\frac{\partial nc}{\partial n_i}\right)_{T,\underline{V},n_{i\neq i}} = 2\sum_i x_i c_{ij} - c \quad \text{.....Eqn. 15.29}$$

$$\left(\frac{\partial(b\rho)}{\partial n_i}\right)_{T,\underline{V},n_{j\neq i}} = \frac{1}{\underline{V}}\left(\frac{\partial(nb)}{\partial n_i}\right)_{T,\underline{V},n_{j\neq i}} = \frac{1}{\underline{V}}\left(\frac{\partial nb}{\partial n_i}\right)_{T,\underline{V},n_{i\neq i}} = \frac{b_i}{\underline{V}} \quad \text{.....using Eqn. 15.22}$$

second term in $\ln\hat{\varphi}_i$ becomes equal to $\dfrac{4cn}{\underline{V}}\dfrac{b_i}{1-b\rho} = \dfrac{b_i}{b}\left(\dfrac{4cb\rho}{1-b\rho}\right) = \dfrac{b_i}{b}(Z-1)$

$$\Rightarrow \ln\hat{\varphi}_j = 4\left(c - 2\sum_i x_i c_{ij}\right)\ln(1-b\rho) + \frac{b_j}{b}(Z-1) - \ln Z$$