Problem Set 12 - Solutions

Problem 10.53

The molar volume $(cm^3\ mol^{-1})$ of a binary liquid mixture at T and P is given by:

$$V = 120\, x_1 + 70\, x_2 + (15\, x_1 + 8\, x_2)\, x_1\, x_2$$

(a) Find expressions for the partial molar volumes of species 1 and 2 in terms of x_1.

(b) Show that the given equation for V is recovered when these expressions are combined using Eq. 10.11.

(c) Show that these expressions satisfy Eq. 10.14.

(d) Show that $\left(d\,\overline{V}_1 / dx_1\right)_{x_1=1} = \left(d\,\overline{V}_2 / dx_1\right)_{x_1=0} = 0$.

(e) Make a plot of V, $\overline{V}_1$, and $\overline{V}_2$ versus x_1.

(f) Label points V_1, V_2, $(\overline{V}_1)_{x_1 \to 0}$, and $(\overline{V}_2)_{x_2 \to 0}$ on the plot and show their values.

Common Information

In[ ]:=
```
Clear["Gloabal`*"]
```

In[ ]:=
```
x2 = 1 - x1;
```

In[ ]:=
```
V = 120 x1 + 70 x2 + (15 x1 + 8 x2) x1 x2 // Expand
```

Out[ ]=

$$70 + 58\, x1 - x1^2 - 7\, x1^3$$

Part (a) - Find expressions for the partial molar volumes of species 1 and 2 in terms of x_1

In[ ]:=
```
V1bar = V + x2 * ∂x1 V // Expand (*Eq. 10.15, L34 Slide 16)*)
```

Out[ ]=

$$128 - 2\, x1 - 20\, x1^2 + 14\, x1^3$$

The partial molar volume of component 1 is $\overline{V}_1 = 128 - 2\, x1 - 20\, x1^2 + 14\, x1^3$. //ANS

In[ ]:=
```
V2bar = V - x1 * ∂x1 V // Expand (*Eq. 10.15, L34 slide 16*)
```

Out[ ]=

$$70 + x1^2 + 14\, x1^3$$

The partial molar volume of component 2 is $\overline{V}_2 = 70 + x1^2 + 14\, x1^3$. //ANS

Part (b) - Show that the given equation for V is recovered when these expressions (for $\overline{V}_1$ and $\overline{V}_2$) are combined using Eq. 10.11

In[ ]:=
```
ansb = x1 * V1bar + x2 * V2bar // Simplify (*Eq. 10.11, L34, slides 15 and 16)*)
```
Out[ ]=

$70 + 58\,x1 - x1^2 - 7\,x1^3$

In[ ]:=
```
ansb == V
```
Out[ ]=

True

Since ansb==V generates “True” output, $x1 * \overline{V}_1 + x2 * \overline{V}_2$ is equal to V, and the original expression for V is recovered. //ANS

Part (c) - Show that these expressions satisfy Eq. 10.14

In[ ]:=
```
x1 * ∂x1 V1bar + x2 * ∂x1 V2bar // Simplify (*Eq. 10.14, L34, slides 15 and 16*)
```
Out[ ]=

0

Since $x1 * \partial_{x1} \overline{V}_1 + x2 * \partial_{x1} \overline{V}_2 = 0$, Equation 10.14 is satisfied. //ANS

Part (d) - Show that $(d\,\overline{V}_1 / dx1)_{x1=1} = (d\,\overline{V}_2 / dx1)_{x1=0} = 0$

The ReplaceAll function (/.) is used to substitute x1→1 into $d\,\overline{V}_1/dx1$ and x1→0 into $d\,\overline{V}_2/dx1$:

In[ ]:=
```
∂x1 V1bar /. x1 → 1
```
Out[ ]=

0

In[ ]:=
```
∂x1 V2bar /. x1 → 0
```
Out[ ]=

0

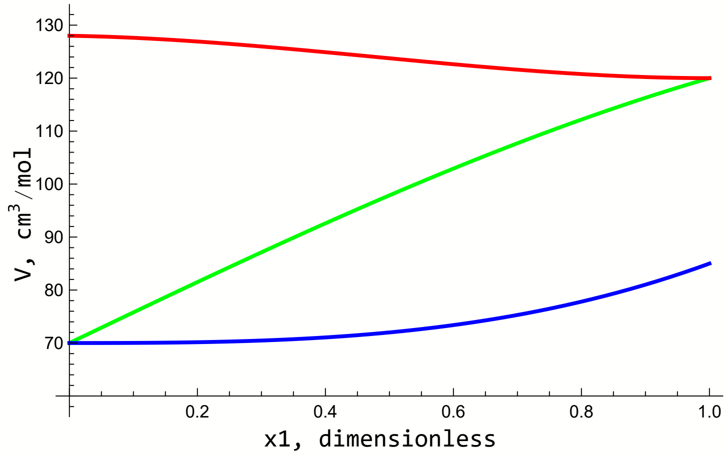
Therefore $(d\,\overline{V}_1 / dx1)_{x1=1} = 0$ and $(d\,\overline{V}_2 / dx1)_{x1=0} = 0$, as requested. //ANS

Part (e) - Make a plot of V, $\overline{V}_1$, and $\overline{V}_2$ versus x_1

In[ ]:=
```
p1 = Plot[V, {x1, 0, 1}, PlotStyle → Blue];
p2 = Plot[V1bar, {x1, 0, 1}, PlotStyle → Red ];
p3 = Plot[V2bar, {x1, 0, 1}, PlotStyle → Green ];
```
In[ ]:=
```
p10 = Show[p1, p2, p3, PlotRange → {{0, 1}, {60, 130}}, AxesOrigin → {0, 60}];
```

In[ ]:=
```
Labeled[p10, {"V, cm³/mol", "x1, dimensionless"},
  {Left, Bottom}, RotateLabel → {True, False}]
```

Out[ ]=



The required plot is shown above. //ANS

Part (f) - Label the points V_1, V_2, $(\overline{V}_1)_{x_1\to0}$, and $(\overline{V}_2)_{x_2\to0}$ on the plot and show their values

Use the provided template.

PLOT FUNCTIONS

In[ ]:=
```
f = V;
g = V1bar;
h = V2bar;
```

DEFINE THE PARTS OF THE LABELS

In[ ]:=
```
part1 = "V₁";
part2 = f /. x1 → 1;

part3 = "V₂";
part4 = f /. x1 → 0;

part5 = "(V̄₁)x₁→0";
part6 = g /. x1 → 0;

part7 = "(V̄₂)x₂→0";
part8 = h /. x1 → 1;
```

BUILDING THE LABELS

Connect the parts together to form labels.

```
(*label1=StringTemplate["`a`=`b`"][<|"a"→part1,"b"→part2|>];
label2=StringTemplate["`a`=`b`"][<|"a"→part3,"b"→part4|>];
label3=StringTemplate["`a`=`b`"][<|"a"→part5,"b"→part6|>];
label4=StringTemplate["`a`=`b`"][<|"a"→part7,"b"→part8|>];*)
```

```
In[∘]:= label1 = StringForm["`1`=`2`", part1, part2];
label2 = StringForm["`1`=`2`", part3, part4];
label3 = StringForm["`1`=`2`", part5, part6];
label4 = StringForm["`1`=`2`", part7, part8];
```

PLOTS

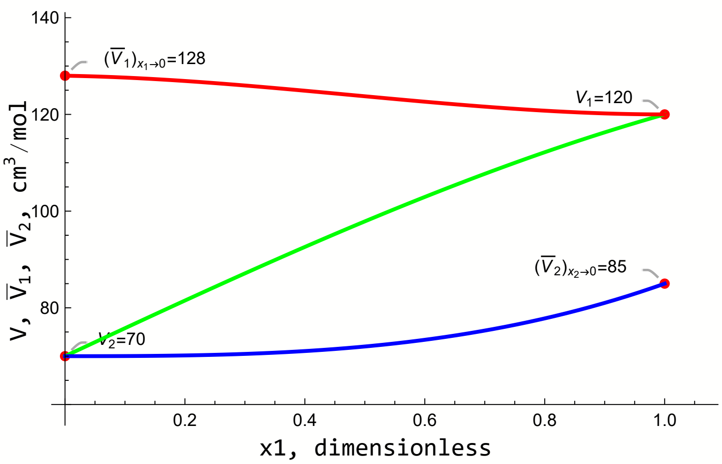
PLOT OF LABELS AND POINTS

```
In[∘]:= (*LABEL AND COORDINATE LISTS*)
coordinateList = {{1, part2}, {0, part4}, {0, part6}, {1, part8}};
labelList = {label1, label2, label3, label4};

(*INDIVIDUAL PLOTS*)
p1 = Plot[f, {x1, 0, 1}, PlotStyle → Blue];
p2 = Plot[g, {x1, 0, 1}, PlotStyle → Red];
p3 = Plot[h, {x1, 0, 1}, PlotStyle → Green ];

(*PLOT OPTIONS*)
option1 = PlotStyle → Red;
option2 = PlotMarkers → {Automatic, 9};
option3 = PlotRange → {{0, 1}, {60, 130}};
option4 = AxesOrigin → {0, 60};
option5 = {"V, V̄1, V̄2, cm3/mol", "x1, dimensionless"};
option6 = {Left, Bottom};
option7 = RotateLabel → {True, False};

(*POINT/LABEL PLOT*)
p4 = With[
   {pts = coordinateList,
    labels = labelList}, ListPlot[Thread[Callout[pts, labels]], option1, option2]];
```

PLOT OF LABELED FUNCTION CURVES

In[∘]:=
```
(*COMBINED PLOT*)
p11 = Show[p4, p1, p2, p3, option3, option4];

(*PLOT WITH AXIS LABELS*)
Labeled[p11, option5, option6, option7]
```

Out[∘]=



Problem 10.18

Estimate the fugacity of isobutylene gas at 280 °C and

(a) 1 bar

(b) 20 bar, and

(c) 100 bar.

Use the SRK equation of state.

In[ ]:=
```
Clear["Global`*"]
```

Part (a)

In[ ]:=
```
(*Temperature and Pressure*)
t = 280 + 273.15; (*K*)
p = 1.; (*bar*)

(*Isobutylene Properties from Table B.1, p.664*)
tc = 417.9; (*K*)
pc = 40.00; (*bar*)
ω = 0.194; (*not used in RK EOS*)

(*Reduced T and P*)
tr = t / tc; (*reduced temperature*)
pr = p / pc; (*reduced pressure*)

(*Equation of state supporting information from Table 3.1 page 100*)
σ = 1;
ϵ = 0;
Ω = 0.08664;
Ψ = 0.42748;
α[x_] = (1 + (0.480 + 1.574 * ω - 0.176 * ω^2) * (1 - Sqrt[x]))^2; (*Table 3.1*)

(*Equation of state*)
β = Ω * pr / tr; (*eq 3.50*)
q[x_] = (Ψ * α[x]) / (Ω * x); (*eq 3.50*)
eq1 = z == (1 + β - q[tr] * β * (z - β) / ((z + ϵ * β) * (z + σ * β))); (*Eq. 3.48*)

(*Solve for Z*)
Z = z /. Solve[eq1, z, Reals][[1, 1]] // Quiet; (*//ANS*)

(*Solve for the Integral*)
I = 1 / (σ - ϵ) * Log[(Z + σ * β) / (Z + ϵ * β)]; (*Eq. 13.72*)

(*Solve for Fugacity Coefficient*)
ϕ = Exp[Z - 1 - Log[Z - β] - q[tr] * I]; (*Eq. 13.85*)

(*Solve for Fugacity*)
f = ϕ * p
```

Out[ ]=
```
0.9968878
```

At P = 1 bar, f = 0.996888 bar. //ANS

Part (b)

Pressure is re-entered and all terms dependent on pressure must be re-calculated.

In[ ]:=
```
(*Update Pressure*)
p = 20.; (*bar*)

(*Update Reduced Pressure*)
pr = p / pc; (*reduced pressure*)

(*Update equation of state*)
β = Ω * pr / tr; (*eq 3.50*)
q[x_] = (Ψ * α[x]) / (Ω * x); (*eq 3.50*)
eq1 = z == (1 + β - q[tr] * β * (z - β) / ((z + ϵ * β) * (z + σ * β))); (*Eq. 3.48*)

(*Re-solve for Z*)
Z = z /. Solve[eq1, z, Reals][[1, 1]] // Quiet; (*//ANS*)

(*Re-solve for the Integral*)
I = 1/(σ - ϵ) * Log[(Z + σ * β)/(Z + ϵ * β)]; (*Eq. 13.72*)

(*Re-solve for Fugacity Coefficient*)
ϕ = Exp[Z - 1 - Log[Z - β] - q[tr] * I]; (*Eq. 13.85*)

(*Re-solve for Fugacity*)
f = ϕ * p
```

Out[ ]=

18.79554

At P = 20 bar, f = 18.7955 bar. //ANS

Part (c)

In[ ]:=
```
(*Update Pressure*)
p = 100.; (*bar*)

(*Update Reduced Pressure*)
pr = p / pc; (*reduced pressure*)

(*Update equation of state*)
β = Ω * pr / tr; (*eq 3.50*)
q[x_] = (Ψ * α[x]) / (Ω * x); (*eq 3.50*)
eq1 = z == (1 + β - q[tr] * β * (z - β)/((z + ϵ * β) * (z + σ * β))); (*Eq. 3.48*)

(*Re-solve for Z*)
Z = z /. Solve[eq1, z, Reals]〚1, 1〛 // Quiet; (*//ANS*)

(*Re-solve for the Integral*)
I = 1/(σ - ϵ) * Log[(Z + σ * β)/(Z + ϵ * β)]; (*Eq. 13.72*)

(*Re-solve for Fugacity Coefficient*)
ϕ = Exp[Z - 1 - Log[Z - β] - q[tr] * I]; (*Eq. 13.85*)

(*Re-solve for Fugacity*)
f = ϕ * p
```

Out[ ]=

74.8573

At P = 100 bar, f = 74.8573 bar. //ANS

At higher pressure, molecules are forced closer together and thus experience greater IMFs and decreasing the fugacity.

Problem 10.21

From the data in the steam tables, determine a good estimate of f/f^{sat} for liquid water at 150°C and 150 bar, where f^{sat} is the fugacity of saturated liquid at 150°C.

SOLUTION

Use the Poynting factor from Eq. 10.44.
Use Table E.1 (saturated steam) on pages 697-703.
Table E.1 is for saturated steam in SI units (P in bar, T in °C, V in cm^3/g).
The temperature is given as 150°C - lookup in table on page 700.
P^{sat} is 4.76 bar - lookup.
V^{sat} = 1.091 g/cm^3 - lookup.
Assume liquid is incompressible so that $V_i^{sat} = V^{sat}$.

In[ ]:=
```
Psat = 4.76; (*bar*)
MW = 18.015; (*g/mol*)
Vil = 1.091 * MW; (*molar volume of liquid; units cm^3/g * g/mol = cm^3/mol *)
T = 150 + 273.15 ; (*K*)
P = 150; (*bar, given*)
(*Gas constant in (bar*cm^3)/(mol*K) from Table A.2*)
R = 83.14;
```

Poynting factor = f/f^{sat}:

```
(*Poynting factor = f/f^sat*)
```

In[ ]:=
```
PoyntingFactor = Exp[(Vil * (P - Psat))/(R * T)]
```

Out[ ]=

1.084 524

The Poynting factor is 1.084524. //ANS