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

(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.

Solution - Part (a)

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

```
In[∘]:= x2 = 1 - x1;
```

```
In[∘]:= V = Expand[120 x1 + 70 x2 + (15 x1 + 8 x2) x1 x2]
Out[∘]=
70 + 58 x1 - x1^2 - 7 x1^3
```

Partial molar volume of component 1. Use Eq. 10.15 for $\overline{V}_1$ (Lesson 34, Slide 16):

```
In[∘]:= V̄1 = Expand[V + x2 * ∂x1 V] (*//ANS*)
Out[∘]=
128 - 2 x1 - 20 x1^2 + 14 x1^3
```

Partial molar volume of component 2. Use Eq. 10.15 for $\overline{V}_2$ (Lesson 34, slide 16):

```
In[∘]:= V̄2 = Expand[V - x1 * ∂x1 V] (*//ANS*)
Out[∘]=
70 + x1^2 + 14 x1^3
```

Solution - 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 (Lesson 34, slides 15 and 16).

In[ ]:=
```
ansb = Expand[x1 * V̄1 + x2 * V̄2]
```
Out[ ]=
```
70 + 58 x1 - x1^2 - 7 x1^3
```
In[ ]:=
```
ansb == V
```
Out[ ]=
```
True
```
Since $x1*\overline{V}_1 + x2*\overline{V}_2$ is equal to V (shown with "True" output), the original expression is recovered. //ANS

Solution - Part (c)

Show that these expressions satisfy Eq. 10.14 (Lesson 34, slides 15 and 16).

In[ ]:=
```
Expand[x1 * ∂x1 V̄1 + x2 * ∂x1 V̄2]
```
Out[ ]=
```
0
```
Since $x1*\partial_{x1}\overline{V}_1 + x2*\partial_{x1}\overline{V}_2 = 0$, equation 10.14 is satisfied. //ANS

Solution - Part (d)

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

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

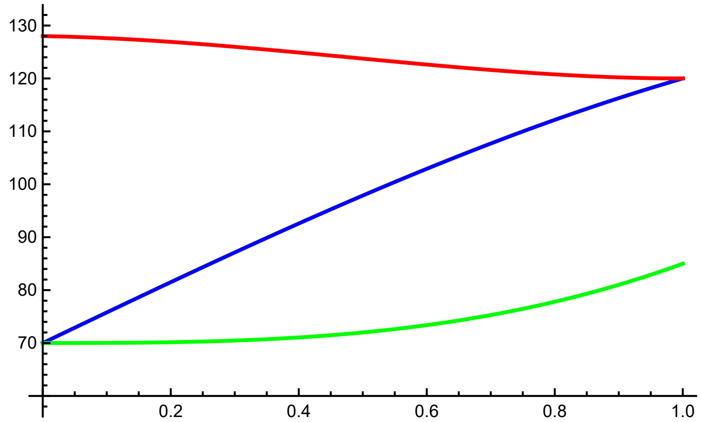
In[ ]:=
```
∂x1 V̄1 /. x1 → 1
```
Out[ ]=
```
0
```
In[ ]:=
```
∂x1 V̄2 /. x1 → 0
```
Out[ ]=
```
0
```
Therefore $\left(d\,\overline{V}_1/\mathrm{dx1}\right)_{x1=1} = 0$ and $\left(d\,\overline{V}_2/\mathrm{dx1}\right)_{x1=0} = 0$, as required. //ANS

Solution - Part (e)

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

In[ ]:=
```
V1b = V̄1; (*Rename V̄1 and V̄2 for "Plot."*)
V2b = V̄2; (*Plot cannot handle the subscript.*)
```
In[ ]:=
```
p1 = Plot[V, {x1, 0, 1}, PlotStyle → Blue];
p2 = Plot[V1b, {x1, 0, 1}, PlotStyle → Red ];
p3 = Plot[V2b, {x1, 0, 1}, PlotStyle → Green ];
```

```
In[◦]:= Show[p1, p2, p3, PlotRange → {{0, 1}, {60, 130}}, AxesOrigin → {0, 60}]
Out[◦]=
```



The required plot is shown above. //ANS

Solution - Part (f)

Label the 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.

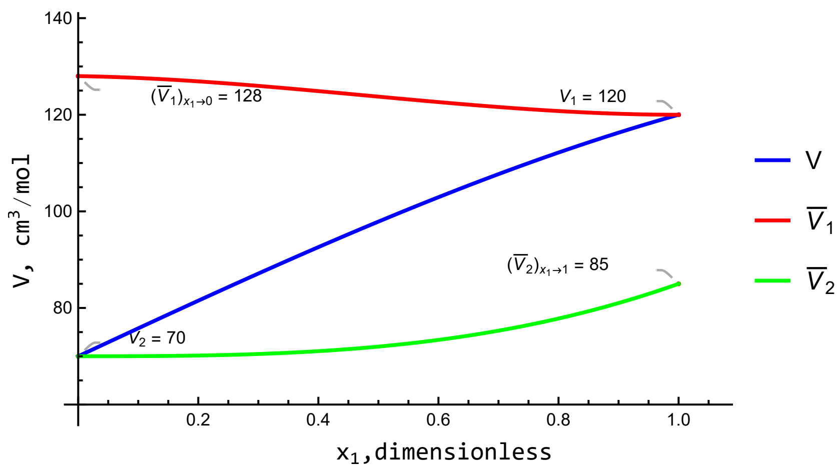
```
In[◦]:= var1 = "V₁";
var2 = V /. x1 → 1;
var3 = "V₂";
var4 = V /. x1 → 0;
var5 = "(V̄₁)x₁→0";
var6 = V̄₁ /. x1 → 0;
var7 = "(V̄₂)x₁→1";
var8 = V̄₂ /. x1 → 1;

lab1 = StringForm["`1` = `2`", var1, var2];
lab2 = StringForm["`1` = `2`", var3, var4];
lab3 = StringForm["`1` = `2`", var5, var6];
lab4 = StringForm["`1` = `2`", var7, var8];

p1 = Plot[V, {x1, 0, 1}, PlotStyle → Blue, PlotLegends → {"V"}];
p2 = Plot[V1b, {x1, 0, 1}, PlotStyle → Red, PlotLegends → {"V̄₁"}];
p3 = Plot[V2b, {x1, 0, 1}, PlotStyle → Green, PlotLegends → {"V̄₂"}];
p4 = With[
   {pts = {{1, V /. x1 → 1}, {0, V /. x1 → 0}, {0, V̄₁ /. x1 → 0}, {1, V2b /. x1 → 1}},
    labels = {lab1, lab2, lab3, lab4}},
   ListPlot[Thread[Callout[pts, labels]], PlotStyle → Red, PlotMarkers → {Automatic, 5}]];
```

```
In[ ]:= Labeled[Show[p4, p1, p2, p3, PlotRange → {{0, 1}, {60, 130}}, AxesOrigin → {0, 60}],
         {"V, cm³/mol", "x₁,dimensionless"}, {Left, Bottom}, RotateLabel → True]
```

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.

Solution - Part (a)

In[∘]:=
```
Quit[];
```

In[∘]:=
```
tc = 417.9; (*K*) (*Table B.1*)
pc = 40.00; (*bar*)
ω = 0.194;
```

In[∘]:=
```
t = 280 + 273.15; (*K*)
P = 1; (*bar*)
tr = t / tc;
pr = P / pc;
```

In[∘]:=
```
α = (1 + (0.480 + 1.574 * ω - 0.176 * ω^2) * (1 - Sqrt[tr]))^2; (*Table 3.1*)
σ = 1;
ϵ = 0;
Ω = 0.08664;
Ψ = 0.42748;
β = Ω * pr/tr; (*Eq. 3.50*)
q = (Ψ * α)/(Ω * tr); (*Eq. 3.51*)
eq1 = Z == 1 + β - q * β * (Z - β)/((Z + ϵ * β) * (Z + σ * β)); (*Eq. 3.48*)
```

In[∘]:=
```
Z1 = Z /. Quiet[Solve[eq1, Z, Reals]][[1]]
```

Out[∘]=
```
0.996883339738
```

In[∘]:=
```
I = 1/(σ - ϵ) * Log[(Z1 + σ * β)/(Z1 + ϵ * β)]; (*Eq. 13.72*)
```

In[∘]:=
```
ϕ = Exp[Z1 - 1 - Log[Z1 - β] - q * I] (*Eq. 13.85*)
```

Out[∘]=
```
0.996887803989
```

In[ ]:=
```
f = ϕ * P
```
Out[ ]=
```
0.996887803989
```

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

Solution - Part (b)

In[ ]:=
```
P = 20; (*bar*)
pr = P / pc;
```
$$\beta = \Omega * \frac{pr}{tr};$$

In[ ]:=
$$eq1 = Z == 1 + \beta - q * \beta * \frac{(Z - \beta)}{(Z + \epsilon * \beta) * (Z + \sigma * \beta)};$$
```
Z2 = Z /. Quiet[Solve[eq1, Z, Reals]][[1]];
```
$$I = \frac{1}{\sigma - \epsilon} * Log\left[\frac{Z2 + \sigma * \beta}{Z2 + \epsilon * \beta}\right];$$
```
Clear[ϕ];
ϕ = Exp[Z2 - 1 - Log[Z2 - β] - q * I];
f = ϕ * P
```
Out[ ]=
```
18.7955351122
```

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

Solution - Part (c)

In[ ]:=
```
P = 100; (*bar*)
pr = P / pc;
```
$$\beta = \Omega * \frac{pr}{tr};$$

In[ ]:=
$$eq1 = Z == 1 + \beta - q * \beta * \frac{(Z - \beta)}{(Z + \epsilon * \beta) * (Z + \sigma * \beta)};$$
```
Z3 = Z /. Quiet[Solve[eq1, Z, Reals]][[1]];
```
$$I = \frac{1}{\sigma - \epsilon} * Log\left[\frac{Z3 + \sigma * \beta}{Z3 + \epsilon * \beta}\right];$$
```
ϕ = Exp[Z3 - 1 - Log[Z3 - β] - q * I];
f = ϕ * P
```
Out[ ]=
```
74.857304975
```

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

At higher pressure, molecules are forced closer together and thus experience greater IMFs. The affect of increasing IMFs is to decrease pressure.

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 data from Steam Table E.1 on pages 697-703.
Table E.1 is for saturated steam in SI units.
The temperature is 150 °C - lookup in table on page 700.
Psat is 4.76 bar - lookup in table on page 698.

```
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*)
PoyntingFactor = Exp[(Vil * (P - Psat))/(R * T)]
1.08452391228
```

The Poynting factor is 1.08452. //ANS