Problem 10.53

The molar volume $(\mathrm{cm}^3\ \mathrm{mol}^{-1})$ 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 $(d\overline{V}_1/\mathrm{dx}_1)_{x_1=1} = (d\overline{V}_2/\mathrm{dx}_1)_{x_1=0} = 0$.

(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 to Part (a):

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

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

Out[ ]=

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

```
(*Partial molar volume of component 1*)
(*Use Eq. 10.15 for V̄1 (Lesson 34 Slide 16)*)
```

In[ ]:=
```
V̄1 = Expand[V + x2 * ∂x1 V] (*//ANS*)
```

Out[ ]=

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

```
(*Partial molar volume of component 2*)
(*Use Eq. 10.16 for V̄2 (Lesson 34 Slide 16)*)
```

In[ ]:=
```
V̄2 = Expand[V - x1 * ∂x1 V] (*//ANS*)
```

Out[ ]=

$70 + \mathrm{x1}^2 + 14\,\mathrm{x1}^3$

Solution to Part (b):

```
(*Eq. 10.11: Lesson 34 slides 15 and 16*)
```

In[ ]:=
```
ansb = Expand[x1 * V̄1 + x2 * V̄2]
```

Out[ ]=

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

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

Out[ ]=

True

```
(*Since x1*V̄1+
  x2*V̄2 is equal to V (with "True") the original expression is recovered.//ANS*)
```

Solution to Part (c):

```
(*Eq. 10.14: Lesson 34 slides 15 and 16 *)
```

(*$x_1 d\overline{M}_1 + x_2 d\overline{M}_2 = 0$ → divide both terms by dx_1 → $x_1 \frac{d\overline{M}_1}{dx_1} + x_2 \frac{d\overline{M}_2}{dx_1} = 0$ *)

In[ ]:= Expand$\left[x1 * \partial_{x1}\overline{V}_1 + x2 * \partial_{x1}\overline{V}_2\right]$

Out[ ]=

```
0
```

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

Solution to Part (d):

(*The /. operator substitutes x1→1 into $\partial_{x1}\overline{V}_1$.*)

In[ ]:= $\partial_{x1}\overline{V}_1$ /. x1 → 1

Out[ ]=

```
0
```

In[ ]:= $\partial_{x1}\overline{V}_2$ /. x1 → 0

Out[ ]=

```
0
```

(* $\left(d\overline{V}_1/dx_1\right)_{x_1=1} = 0$ and $\left(d\overline{V}_2/dx_1\right)_{x_1=0} = 0$. //ANS*)

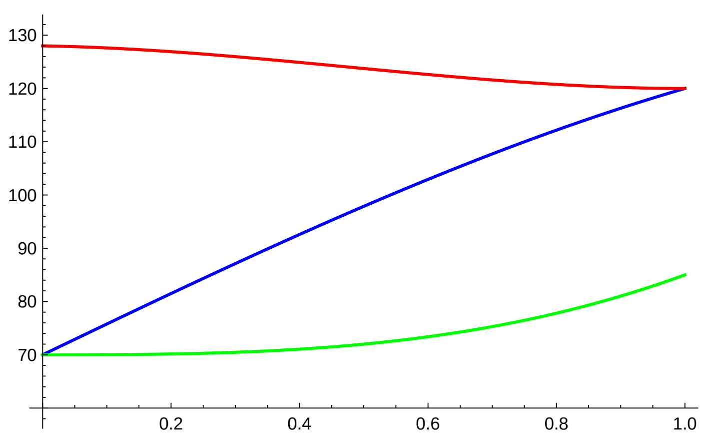
Solution to Part (e):

In[ ]:= V1b = $\overline{V}_1$; (*Rename $\overline{V}_1$ and $\overline{V}_2$ for "Plot."*)
V2b = $\overline{V}_2$; (*Plot cannot seem to 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 to Part (f):

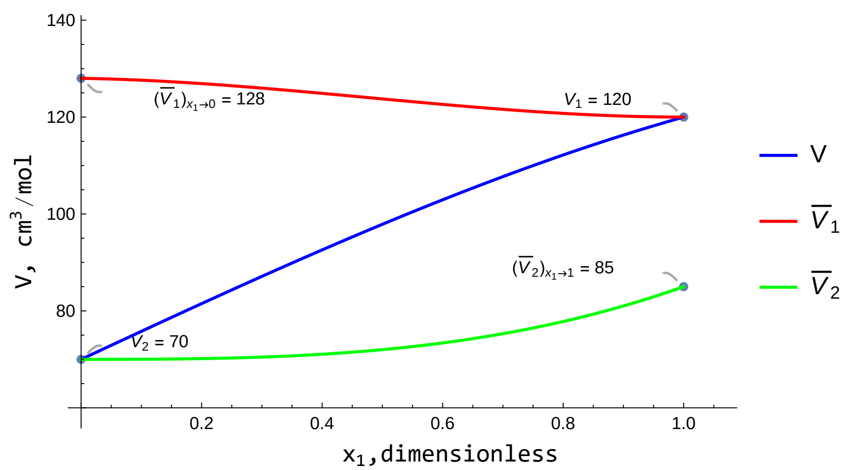
In[◦]:=
```
var1 = "V1";
var2 = V /. x1 → 1;
var3 = "V2";
var4 = V /. x1 → 0;
var5 = "(V̄1)x1→0";
var6 = V̄1 /. x1 → 0;
var7 = "(V̄2)x1→1";
var8 = V̄2 /. x1 → 1;

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]], PlotMarkers → {Automatic, 5}]];
```

In[◦]:=
```
Labeled[Show[p4, p1, p2, p3, PlotRange → {{0, 1}, {60, 130}}, AxesOrigin → {0, 60}],
 {"V, cm^3/mol", "x1,dimensionless"}, {Left, Bottom}, RotateLabel → True]
```

Out[◦]=



Problem 10.18

Estimate the fugacity of isobutylene gas at 280 deg C and

(a) 1 bar
(b) 20 bar, and
(c) 100 bar.

Solution

```
(*Table B.1*)
(*tc=417.9 K*)
(*pc=40.00 bar*)
(*ω=0.194*)

(*Table 3.1*)
α = (1 + (0.480 + 1.574 * ω - 0.176 * ω^2) * (1 - Sqrt[t / tc]))^2;
σ = 1;
ϵ = 0;
Ω = 0.08664;
Ψ = 0.42748;
(*Eqs. 3.50, 3.51, and 3.48*)
β = Ω * (p / pc) / (t / tc);
q = (Ψ * α) / (Ω * (t / tc));
eos = 1 + β - q * β * (z - β) / ((z + ϵ * β) * (z + σ * β)) - z;
Z = z /. Solve[eos == 0, z][[3]];
(*Eqs. 3.72 and 3.85*)
I = 1 / (σ - ϵ) * Log[(Z + σ * β) / (Z + ϵ * β)];
ϕ[t_, tc_, p_, pc_, ω_] = Exp[Z - 1 - Log[Z - β] - q * I];
```

```
In[ ]:= p = {1, 20, 100};

In[ ]:= p * ϕ[553.15, 417.9, p, 40, .194]
Out[ ]=
{0.996887803989, 18.7955351122, 74.857304975}
```

```
(*The fugacity at 1, 20, and 100 bar are 0.996888,
18.795535, and 74.857305 bar, respectively.  //ANS*)
```

Problem 10.21

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

Solution:

```
(*Use the Poynting factor from the Equation 10.44*)
(*Use data from Steam Table E.1 pages 697-703*)
(*Table E.1 is for saturated steam in SI units*)
(*Temperature is 150 degC - lookup in table page 700.*)
Psat = 4.76; (*bar; 476 kPa in Table E.1, p. 687*)
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*)
R = 83.14; (* bar*cm^3/(mol*K), from Table A.2*)
```

```
19.654365

423.15
```

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

$$\text{PoyntingFactor} = \text{Exp}\left[\frac{\text{Vil} * (\text{P} - \text{Psat})}{\text{R} * \text{T}}\right]$$

```
1.08452391228
```

```
(*//ANS*)
```