Problem 1: For a lab experiment an amount of 2 litres of an antifreeze solution is required. The solution should consist of 30 mol% methanol in water. Determine the volumes of pure methanol and pure water at 25°C that must be mixed to yield the 2 litres of solution. Partial molar volumes for methanol and water in 30 mol% methanol solution and their pure-species molar volumes, both at 25°C, are,

Methanol (1):	$\overline{V}_1$=38.632 $\frac{\text{cm}^3}{\text{gmol}}$	V_1=40.727 $\frac{\text{cm}^3}{\text{gmol}}$
Water (2):	$\overline{V}_2$=17.765 $\frac{\text{cm}^3}{\text{gmol}}$	V_2=18.068 $\frac{\text{cm}^3}{\text{gmol}}$

What would be the volume if an ideal solution were formed?

Problem 2: What is the change in entropy when 700 litres of CO_2 and 300 litres of N_2, each at 1 bar and 25°C blend to form a gas mixture at the same conditions? Assume ideal gases.

Problem 3: The following expressions have been proposed for the partial molar properties of a particular binary mixture:

$$\overline{M}_1 = M_1 + Ax_2 \qquad\qquad \overline{M}_2 = M_2 + Ax_1$$

Here, parameter A is a constant. Can these expressions possibly be correct? Explain.

Problem 4: The volume change of mixing $\left(\text{in cm}^3.\text{gmol}^{-1}\right)$ for the system ethanol (1) and methy-butyl ether (2) at 25°C is given by the equation

$$\Delta V = x_1 x_2 \left[-1.026 + 0.220 \left(x_1 - x_2\right)\right]$$

Given that V_1=58.63 cm^3.gmol^{-1} and V_2=118.46 cm^3.gmol^{-1}, what volume of mixture is formed when 750 cm^3 of pure species 1 is mixed with 1500 cm^3 of species 2 at 25°C? What would be the volume if an ideal solution were formed?

Problem 5: The molar volume $\left(\text{in cm}^3.\text{gmol}^{-1}\right)$ of a binary liquid mixture at T and P is given by:

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

(a) Find expressions for the partial molar volumes of species 1 and 2 at T and P.

(b) Show that when these expressions are combined in accord with $M = \sum_i x_i \overline{M}_i$, the given equation for V is recovered;

(c) Show that these expressions satisfy the Gibbs-Duhem equation, $\sum_i x_i d\overline{M}_i = 0$;

(d) Show that

$$\left(\frac{d\overline{V}_1}{dx_1}\right)_{x_1=1} = \left(\frac{d\overline{V}_2}{dx_1}\right)_{x_1=0} = 0$$

(e) Plot values of V, $\overline{V}_1$ and $\overline{V}_2$ calculated by the given equation for V and by the equations developed in (a) *vs* x_1. Label points $\overline{V}_1^{\infty}$ and $\overline{V}_2^{\infty}$ and show their values.

Problem 01

For a general solution property,

$$M = \sum_i x_i \bar{M}_i$$

The molar volume of the binary solution is

$$V = x_1 \bar{V}_1 + x_2 \bar{V}_2 = 0.3 \times 38.632 + 0.7 \times 17.765$$

$$V = 24.025 \text{ cm}^3/\text{gmol}$$

Total volume required is $V^t = 2$ litres $= 2000 \text{ cm}^3$

$$\hookrightarrow n = \frac{V^t}{V} = \frac{2000 \text{ cm}^3}{24.025 \text{ cm}^3/\text{gmol}} = 83.2466 \text{ gmol}$$

number of moles

The solution contains 30% methanol + 70% water

(methanol) $n_1 = 0.3 \times n = 24.974$ gmol

(water) $n_2 = 0.7 \times n = 58.273$ gmol

Now we can determine the volume of each species through

$$V_i^t = n_i V_i$$

Volume of pure water and methanol

$$V_1^t = 24.974 \text{ gmol} \times 40.727 \text{ cm}^3/\text{gmol} = 1017.12 \text{ cm}^3 = \underline{1.017 \ l}$$

$$V_2^t = 58.273 \text{ gmol} \times 18.068 \text{ cm}^3/\text{gmol} = 1052.88 \text{ cm}^3 = \underline{1.053 \ l}$$

Ideal solution:

$$V^{t}_{ideal} = V_1^{t} + V_2^{t} = \underline{2.070\ \ell}$$

Problem 2: $\left\{ \begin{array}{l} 700\,l\ CO_2\,(1) \\ 300\,l\ N_2\,(2) \end{array} \right\}$ 1 bar and 25°C

For ideal gas: mole fraction = volume fraction (*)

$CO_2\ (1):\ y_1 = 0.7;\ V_1^t = 0.7\ m^3$

$N_2\ (2):\ y_2 = 0.3;\ V_2^t = 0.3\ m^3$

At $P = 1$ bar and $T = 298.15$ K

$$n = \frac{P}{RT} \sum V_i^t = 40.34 \text{ gmol}$$

$$\Delta S = -nR \sum_i y_i \ln y_i = -40.34\ \cancel{\text{gmol}} \times 8.314 \frac{J}{\cancel{\text{gmol}}\,K} (0.7 \ln 0.7 + 0.3 \ln 0.3)$$

$$\Delta S = 204.876\ J/K$$

mole fraction: $x_i = n_i / n$

Volume fraction: $y_i = V_i / V$

$$x_i = \frac{n_i}{n} = \frac{PV_i/RT}{PV/RT} = \frac{V_i}{V} = y_i$$

Problem 03 :

The Gibbs-Duhem equation at constant T & P

$$x_1 \frac{d\bar{M}_1}{dx_1} + x_2 \frac{d\bar{M}_2}{dx_2} = 0 \Rightarrow \sum_i x_i \, d\bar{M}_i = 0$$

For the given expressions:

$$\bar{M}_1 = M_1 + Ax_2 \therefore \bar{M}_1 = M_1 + A(1-x_1)$$

$$\hookrightarrow \frac{d\bar{M}_1}{dx_1} = -A$$

$$\bar{M}_2 = M_2 + Ax_1 \therefore \frac{d\bar{M}_2}{dx_1} = A$$

Using the GD equation

$$x_1(-A) + \overbrace{x_2}^{1-x_1} A = 0$$

$$-Ax_1 + A - Ax_1 = A - 2Ax_1 = 0$$

$$A = 2Ax_1 \quad (\forall A \neq 0)$$

$$\underline{x_1 = 1/2}$$

Thus these expressions are only valid for a single case when $x_1 = x_2 = 0.5$ $\Rightarrow$ <u>Not</u> correct for a general binary mixture.

Problem 04 : $\left\{ \begin{array}{l} \text{Ethanol (1)} \\ \text{Methyl-butyl ether (2)} \end{array} \right\}$ 25°C

$$\Delta V_{MIX} = x_1 x_2 \left[-1.026 + 0.220 (x_1 - x_2)\right]$$

$V_1 = 58.63 \ cm^3/gmol$

$V_2 = 118.46 \ cm^3/gmol$

V^t ?

V^t_{ideal} ?

$$n_1 = \frac{750 \ cm^3}{V_1} = 12.79 \ gmol$$

$$n_2 = \frac{1500 \ cm^3}{V_2} = 12.66 \ gmol$$

$$n = n_1 + n_2 = 24.45 \ gmol$$

$$x_1 = n_1/n = 0.5026 \ \therefore \ x_2 = 1 - x_1 = 04974$$

$$\Delta V_{MIX} = 05026 \times 04974 \left[-1.026 + 0.220 (05026 - 04974)\right]$$

$$\Delta V_{MIX} = -0.256 \ cm^3/gmol = V^E \ (\text{excess volume})$$

$$V^E = V - \sum x_i V_i$$

$$V = V^E + \sum x_i V_i = -0256 + \left[05026 \times 58.63 + 04974 \times 11846\right]$$

$$V = 88.1334 \ cm^3/gmol$$

$$V^t = V \cdot m = 88.1334 \, \text{cm}^3/\text{gmol} \times 24.45 \, \text{gmol}$$

$$\underline{V^t = 2154.8616 \, \text{cm}^3}$$

For ideal solution:

$$V^t_{ideal} = (x_1 V_1 + x_2 V_2) m$$

$$= [0.5026 \times 58.63 + 0.4974 \times 118.46] \frac{\text{cm}^3}{\text{gmol}} \times 24.45 \, \text{gmol}$$

$$\underline{V^t_{ideal} = 2161.12 \, \text{cm}^3}$$

Problem 05: Binary liquid mixture

(a) $$V = 120x_1 + 70x_2 + (15x_1 + 8x_2)x_1x_2$$

Eliminating $x_2 = 1 - x_1$

$$V = 120x_1 + 70(1-x_1) + [15x_1 + 8(1-x_1)]x_1(1-x_1)$$

$$V = 50x_1 + 70 + [7x_1 + 8][x_1 - x_1^2]$$

$$V = 50x_1 + 70 + 7x_1^2 - 7x_1^3 + 8x_1 - 8x_1^2$$

$$V = 70 + 58x_1 - x_1^2 - 7x_1^3 \qquad (1)$$

The Gibb-Duhen equation at constant $\underline{T}$ & $\underline{P}$ can be expressed as

$$\bar{M}_1 = M + x_2 \frac{dM}{dx_1} \quad ; \quad \bar{M}_2 = M - x_1 \frac{dM}{dx_1}$$

and are used to obtain $\bar{V}_1$ and $\bar{V}_2$. But first we need to calculate

$$\frac{dV}{dx_1} = 58 - 2x_1 - 21x_1^2$$

Thus

$$\bar{V}_1 = 70 + 58x_1 - x_1^2 - 7x_1^3 + (1-x_1)(58 - 2x_1 - 21x_1^2)$$

$$\bar{V}_1 = 70 + \cancel{58}x_1 - x_1^2 - 7x_1^3 + 58 - 2x_1 - 21x_1^2 - \cancel{58}x_1 + 2x_1^2 + 21x_1^3$$

$$\boxed{\bar{V}_1 = 128 - 2x_1 - 20x_1^2 + 14x_1^3} \qquad (2)$$

$$\bar{V}_2 = 70 + 58x_1 - x_1^2 - 7x_1^3 - x_1(58 - 2x_1 - 21x_1^2)$$

$$\boxed{\bar{V}_2 = 70 + x_1^2 + 14x_1^3} \qquad (3)$$

(b) For $M = \sum_i x_i \bar{M}_i$

$$V = \sum x_i \bar{V}_i = x_1(128 - 2x_1 - 20x_1^2 + 14x_1^3) + (1-x_1)(70 + x_1^2 + 14x_1^3)$$

$\boxed{V = 70 + 58x_1 - x_1^2 - 7x_1^3}$ ~ recovered the original eqn.

(c) GD eqn: $\sum_i x_i d\bar{M}_i = 0$

$$x_1 d\bar{V}_1 + x_2 d\bar{V}_2 = 0 \qquad \times (1/dx_1)$$

$$x_1 \frac{d\bar{V}_1}{dx_1} + x_2 \frac{d\bar{V}_2}{dx_1} = 0 \qquad (*)$$

Differentiating $\bar{V}_i$ wrt x_1 (from (2) and (3))

$$\frac{d\bar{V}_1}{dx_1} = -2 - 40x_1 + 42x_1^2$$

$$\frac{d\bar{V}_2}{dx_1} = 2x_1 + 42x_1^2$$

Now in (*)

$$x_1(-2-40x_1+42x_1^2) + (1-x_1)(2x_1+42x_1^2) = 0$$

$$0 = 0$$

↳ this demonstrate the validity of the eqn.

(d) Demonstrate

$$\left(\frac{d\bar{V}_1}{dx_1}\right)_{x_1=1} = \left(\frac{d\bar{V}_2}{dx_1}\right)_{x_1=0} = 0$$

From (c)

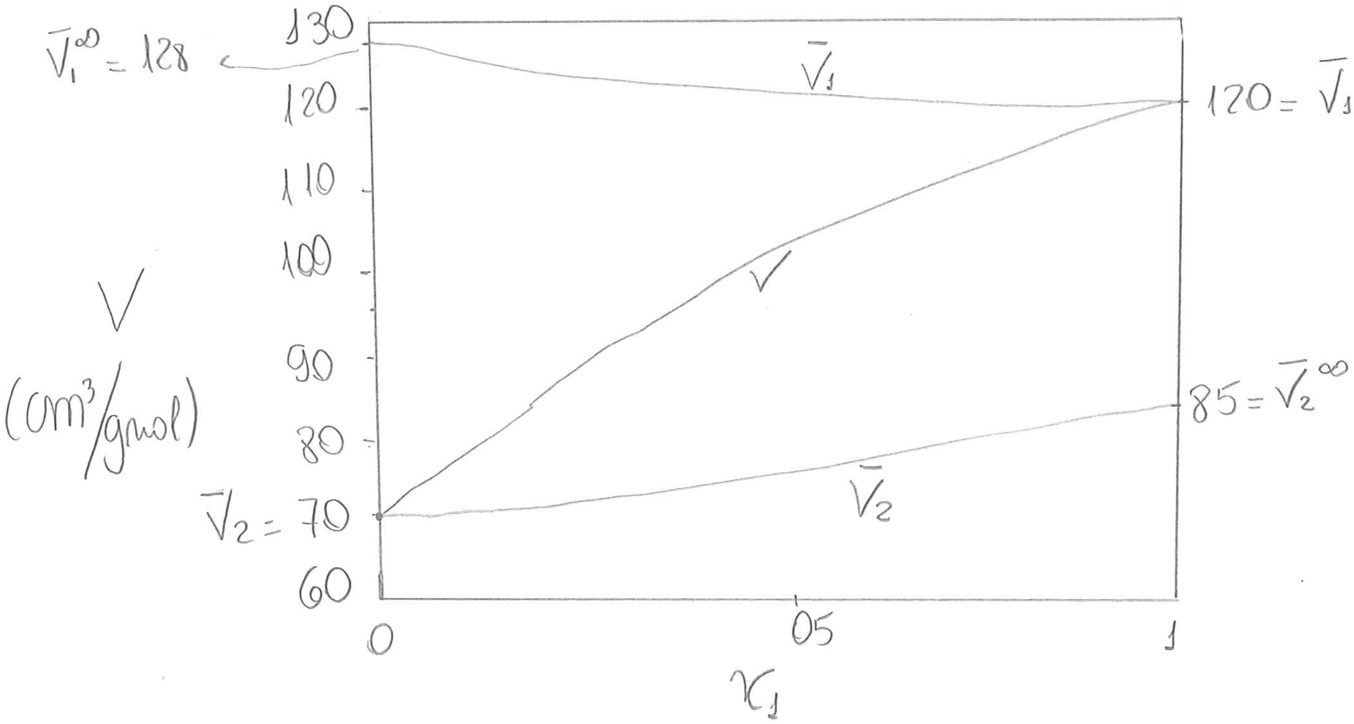
$$\frac{d\bar{V}_1}{dx_1} = -2 - 40x_1 + 42x_1^2$$ using $x_1 = 1$

$$\left[d\bar{V}_1/dx_1\right]_{x_1=1} = 0$$

$$\frac{d\bar{V}_2}{dx_1} = 2x_1 + 42x_1^2$$ using $x_1 = 0$

$$\left[d\bar{V}_2/dx_1\right]_{x_1=0} = 0$$

(e)



	$x_1 = 0.0$	$x_1 = 1.0$
V	70	120
$\bar{V}_1$	128	120
$\bar{V}_2$	70	85