MME 2010
METALLURGICAL THERMODYNAMICS II

Review Problems

The binary system acetonitrile/nitromethane conforms closely to Raoult's law. Vapor pressures for the pure species are given by the following Antoine equations:

ln P_1^{sat}= 14.2724 – 2945.47/(T(C)+224) kPa

ln P_2^{sat}= 14.2043 – 2972.64/(T(C)+209) kPa

Calculate the total pressure for 0.6 weight % acetonitrile containing liquid phase in equilibrium with vapor at room temperature.

$$x_i P_i sat = y_i P$$

For the system n-pentane/n-heptane, the vapor pressures of the pure species are given by
$\ln P_1^{sat} = 13.8183 - 2477.07/(T(C)+233.21)$ kPa
$\ln P_2^{sat} = 13.8587 - 2911.32/(T(C)+216.64)$ kPa
Assuming Raoult's law to describe the vapor/liquid equilibrium states of this system, determine the fraction of the system that is liquid, x_1, and y_1 at 60 C and 1 atm, when the vapor composition of the system is equimolar

$$x_i P_i sat = y_i P$$

How much water must be added to 1000 ml of NiSO4-water solution containing 96% NiSO4.6H2O by volume in order to make a plating solution containing 64% NiSO4.6H2O by volume?
Partial molar volume of NiSO4.6H2O = 98.1 ml for 96% solution, 96.6 ml for 64% solution
Partial molar volume of H2O = 14.5 ml for 96% solution, 17.1 ml for 64% solution

One mole of Pb at 25 C is added to a large amount of Pb-Si liquid alloy with X_{Pb}=0.5 at 473 K. Calculate the activity of lead at 473 K and 1000 K. Partial excess enthalpy and entropy of Pb are -1142.5 J/mole and 1.5 J/mole K respectively

Partial molar entropies of components in an A-B solution are given as S_o-RlnX where X is the mole fraction of component A or B. Determine the entropy change of mixing involving addition of 1 mole of B into A-B solution with X_B= 0.33 initial composition if the addition is made to

a) 3 moles of solution, b)large quantity of solution.

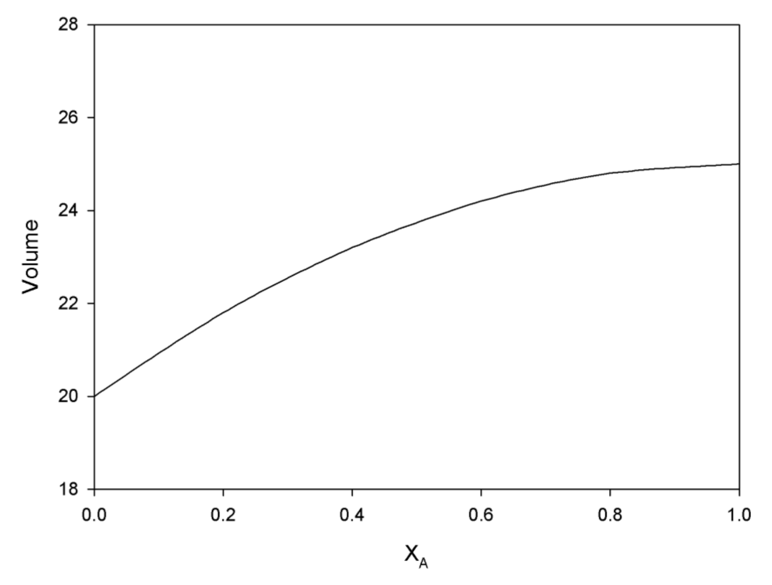
Standard entropies of A and B are 10 J/mol K and 20J/mol K respectively

Total molar enthalpy of mixing for Bi-Cd alloys at 200 C is given as 5000XbiXcd J/mole. Calculate enthalpy change of the system when 1 mole of Cd is added to a solution with X_{Bi}=0.7 if the solution is a) 2 moles, b) large quantity

Calculate the volume change of the process involving the addition of 2 moles of A into an A-B solution with x_A=0.5 initial composition when the initial solution is

a. 2 moles
b. a large quantity

The total volume of the solution is given as a function of x_A in the figure



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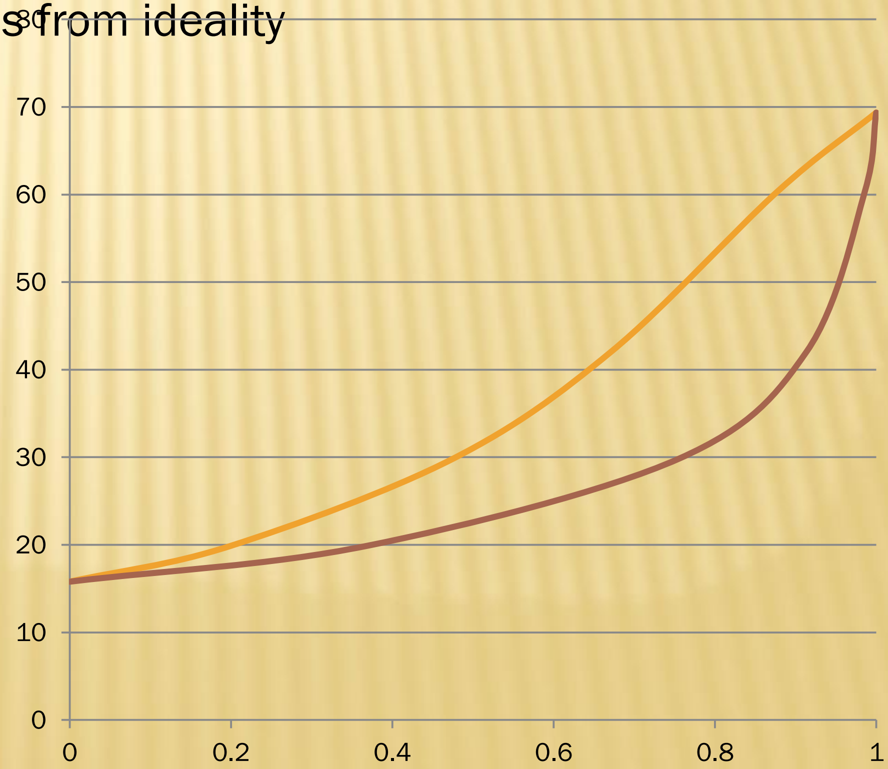
Calculate the total pressure for 0.6 weight % acetonitrile containing liquid phase in equilibrium with vapor at room temperature.

For the binary system of chloroform/dioxane at 50 C, the following vapor-liquid equilibrium data are given:

P kPa	x_1	y_1
15.79	0.000	0.000
19.89	0.200	0.369
29.82	0.475	0.755
42.10	0.672	0.914
60.38	0.878	0.986
69.36	1.000	1.000

Determine whether the system obeys Raoult's law or deviates from it. If there is a deviation from Raoult's law, use modified Raoult's law to quantify it with activity coefficient.

Explain the nature of the intermolecular interaction between chloroform and dioxane molecules for the composition range that the binary system deviates from ideality



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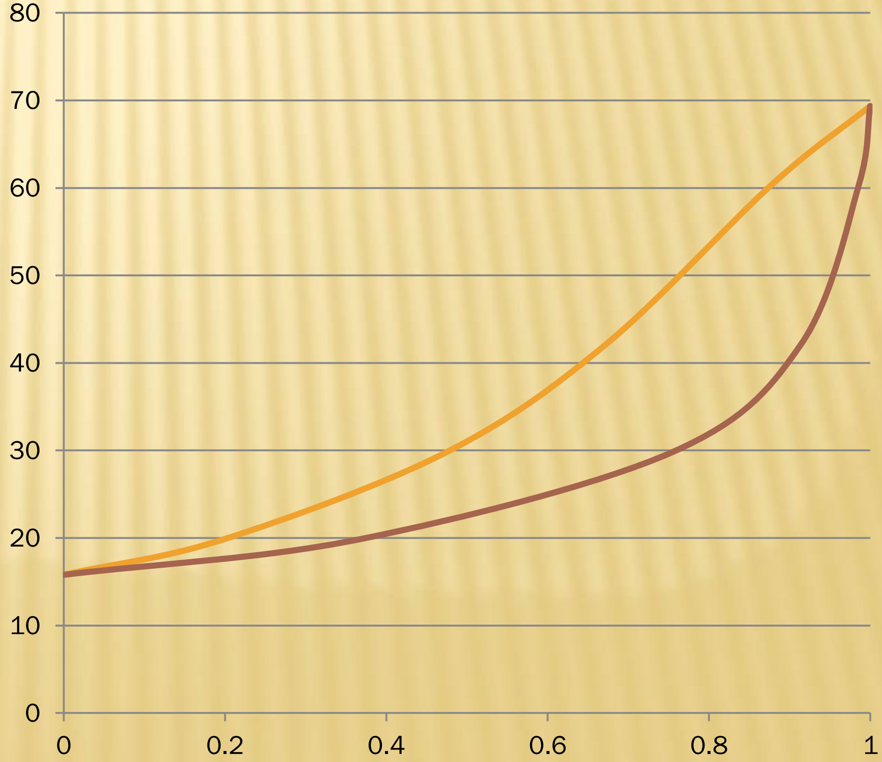
Calculate partial excess entropies and partial excess free energies of chloroform and dioxane at X1= 0.48

Obtain the total excess entropy and Gibbs free energy of the system at that concentration



The excess Gibbs free energy for binary systems comprised of species that are chemically similar is generally expressed as

$G^E/RT=Ax_1x_2$

Determine the value of A for a particular binary system for which the following data are avaliable for a single measurement:

T= 45 C, P= 37 kPa, x_1= 0.398, y_1= 0.428

ln P_1^{sat}= 30.128 – 1497.07/(T(C)+592.594) kPa

ln P_2^{sat}= 31.425 – 1188.15/(T(C)+695.280) kPa

Calculate $\ln\gamma_1$ and $\ln\gamma_2$ values for this single data point

$$\gamma_i x_i P_i sat = y_i P$$

$$\overline{V}_1 = V - x_1 \frac{dV}{dx_1}$$

The excess Gibbs free energy of a binary liquid mixture at a given T and P is given by

$$G^E/RT = (-1.2x_1 - 1.5x_2)\, x_1 x_2$$

Find an expression for $\ln\gamma_1$ and $\ln\gamma_2$ and show that the above equation is recovered from $G^E/RT = \sum x_i \ln\gamma_i$

Show that these equations satisty the Gibbs/Duhem equation ($\sum x_i \, d\ln\gamma_i = 0$)

$$\overline{V}_1 = V - x_1 \frac{dV}{dx_1}$$

The molar volume of a binary liquid mixture at T and P is given by

$$V = 90x_1 + 50x_2 + (6x_1 + 9x_2)x_1x_2$$

Find expressions for the partial molar volumes of species 1 and 2

Show that the above equation is recovered when these expressions are combined

Show that these expressions satisfy the Gibbs/Duhem equation

$$\overline{V}_1 = V - x_1\frac{dV}{dx_1}$$

For a particular binary system at constant T and P, the molar enthalpies of mixtures are represented by the following equation:

$$H = x_1(a_1 + b_1 x_1) + x_2 (a_2 + b_2 x_2)$$

Determine an expression for the partial molar enthalpy of component 1.

Hint: it is not equal to $(a_1 + b_1 x_1)$

$$\overline{H}_1 = H - x_1 \frac{dH}{dx_1}$$

The excess volume of a binary liquid mixture of species 1 and 2 at 25 C and atmospheric pressure is given by the following equation:

$$V^E = x_1x_2\,(30x_1 + 50x_2)\ \text{cm}^3/\text{mol}$$

At the same conditions V_1= 120 cm^3/mol and V_2= 150 cm^3/mol. Determine the partial molar volumes of species 1 and 2 for an equimolar mixture of species.

$$\overline{V}_1{}^E = V^E - x_1\frac{dV^E}{dx_1}$$

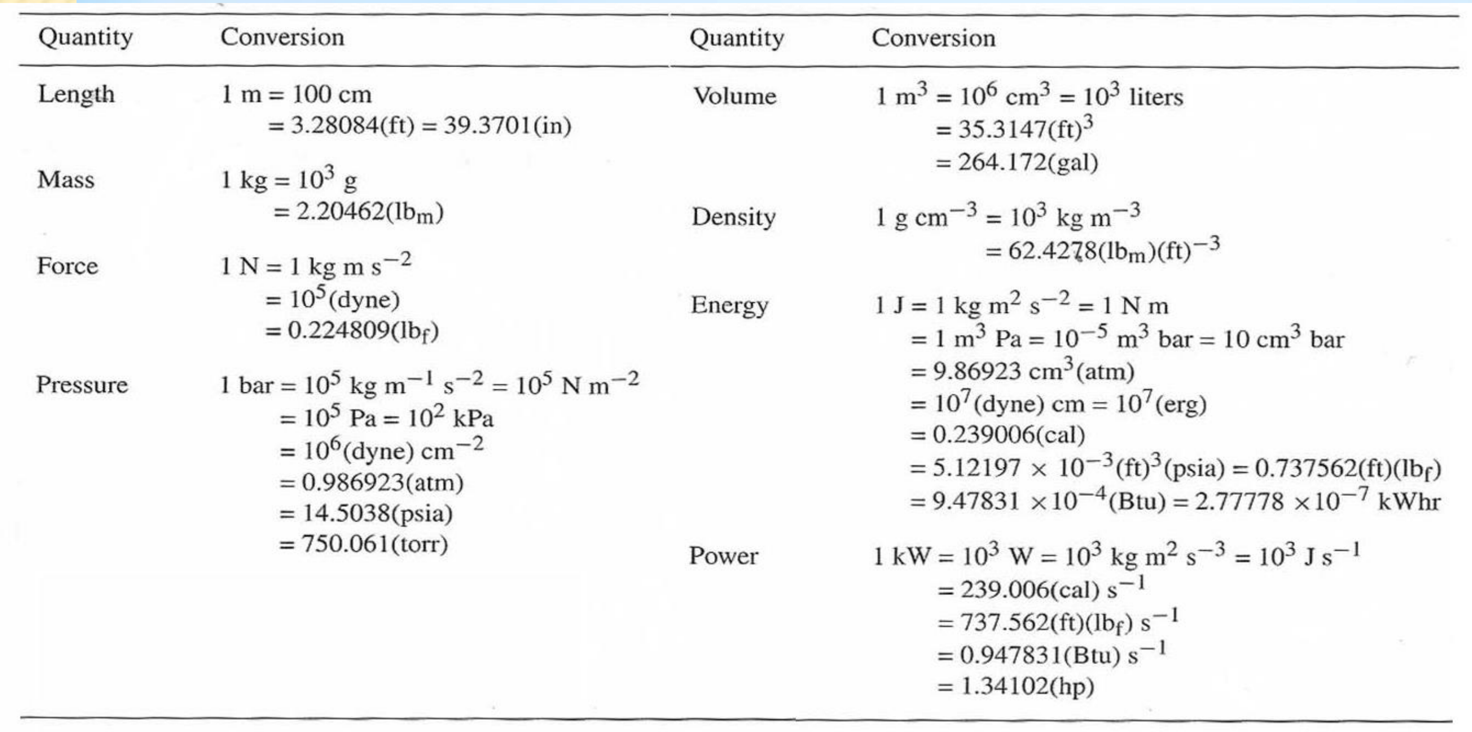
Partial molar volume for one of the components of a binary solution at standard T and P is represented as:

$$\overline{V_A} = 3Xb^2(Xa + 3Xb)\ cm^3$$

Find an expression for the total volume of the system if the molar volume of pure B is 1 cm^3

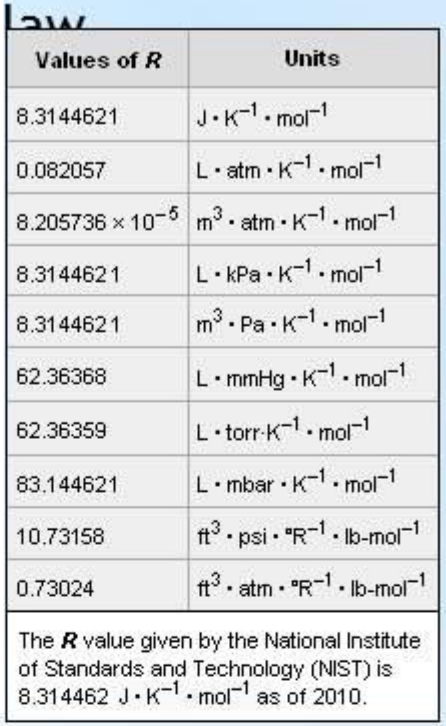
$$\frac{V}{X_B} - {V_B}^o = \int_{X_A=0}^{X_A} \frac{\overline{V}_A dX_A}{{X_B}^2}$$

Gas constant R



Quantity	Conversion	Quantity	Conversion
Length	$1\ \text{m} = 100\ \text{cm}$ $= 3.28084(\text{ft}) = 39.3701(\text{in})$	Volume	$1\ \text{m}^3 = 10^6\ \text{cm}^3 = 10^3$ liters $= 35.3147(\text{ft})^3$ $= 264.172(\text{gal})$
Mass	$1\ \text{kg} = 10^3\ \text{g}$ $= 2.20462(\text{lb}_m)$	Density	$1\ \text{g cm}^{-3} = 10^3\ \text{kg m}^{-3}$ $= 62.4278(\text{lb}_m)(\text{ft})^{-3}$
Force	$1\ \text{N} = 1\ \text{kg m s}^{-2}$ $= 10^5(\text{dyne})$ $= 0.224809(\text{lb}_f)$	Energy	$1\ \text{J} = 1\ \text{kg m}^2\ \text{s}^{-2} = 1\ \text{N m}$ $= 1\ \text{m}^3\ \text{Pa} = 10^{-5}\ \text{m}^3\ \text{bar} = 10\ \text{cm}^3\ \text{bar}$ $= 9.86923\ \text{cm}^3(\text{atm})$ $= 10^7(\text{dyne})\ \text{cm} = 10^7(\text{erg})$ $= 0.239006(\text{cal})$ $= 5.12197 \times 10^{-3}(\text{ft})^3(\text{psia}) = 0.737562(\text{ft})(\text{lb}_f)$ $= 9.47831 \times 10^{-4}(\text{Btu}) = 2.77778 \times 10^{-7}\ \text{kWhr}$
Pressure	$1\ \text{bar} = 10^5\ \text{kg m}^{-1}\ \text{s}^{-2} = 10^5\ \text{N m}^{-2}$ $= 10^5\ \text{Pa} = 10^2\ \text{kPa}$ $= 10^6(\text{dyne})\ \text{cm}^{-2}$ $= 0.986923(\text{atm})$ $= 14.5038(\text{psia})$ $= 750.061(\text{torr})$	Power	$1\ \text{kW} = 10^3\ \text{W} = 10^3\ \text{kg m}^2\ \text{s}^{-3} = 10^3\ \text{J s}^{-1}$ $= 239.006(\text{cal})\ \text{s}^{-1}$ $= 737.562(\text{ft})(\text{lb}_f)\ \text{s}^{-1}$ $= 0.947831(\text{Btu})\ \text{s}^{-1}$ $= 1.34102(\text{hp})$

law



Values of *R*	**Units**
8.3144621	$\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
0.082057	$\text{L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
8.205736×10^{-5}	$\text{m}^3 \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
8.3144621	$\text{L} \cdot \text{kPa} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
8.3144621	$\text{m}^3 \cdot \text{Pa} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
62.36368	$\text{L} \cdot \text{mmHg} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
62.36359	$\text{L} \cdot \text{torr} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
83.144621	$\text{L} \cdot \text{mbar} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
10.73158	$\text{ft}^3 \cdot \text{psi} \cdot {}^\circ\text{R}^{-1} \cdot \text{lb-mol}^{-1}$
0.73024	$\text{ft}^3 \cdot \text{atm} \cdot {}^\circ\text{R}^{-1} \cdot \text{lb-mol}^{-1}$

The ***R*** value given by the National Institute of Standards and Technology (NIST) is $8.314462\ \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ as of 2010.

Volume per gram-mole of ideal gas at 0 °C and 1 atm is 22.414 liters accordin Avogadro's law

Thus $$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} = \frac{1\ atm * 22.414\ liters}{273.15\ degree * mole} = 0.082057\ {}^{liter\ *\ atm}/_{degree\ *\ mole}$$