

MME 2010

METALLURGICAL THERMODYNAMICS II

Partial Properties of Solutions

A total property of a system consisting of multiple substances is represented as

$$nM = \sum n_i M_i$$

If the system consists of a liquid mixture comprised of molecules of the same size and equal forces between, like a solid mixture, the total property is the same:

$$nM = \sum n_i M_i$$

Ideal solution is such a liquid behaving like a solid mixture

In other words, the components of the ideal solution avoid intimate mixing

In contrast, real solutions consist of interacting chemical species and their total system property is apportioned or shared by individual components as their partial properties

$$nM = \sum n_i \bar{M}_i$$

Apportioning of system properties as a puzzle analogy

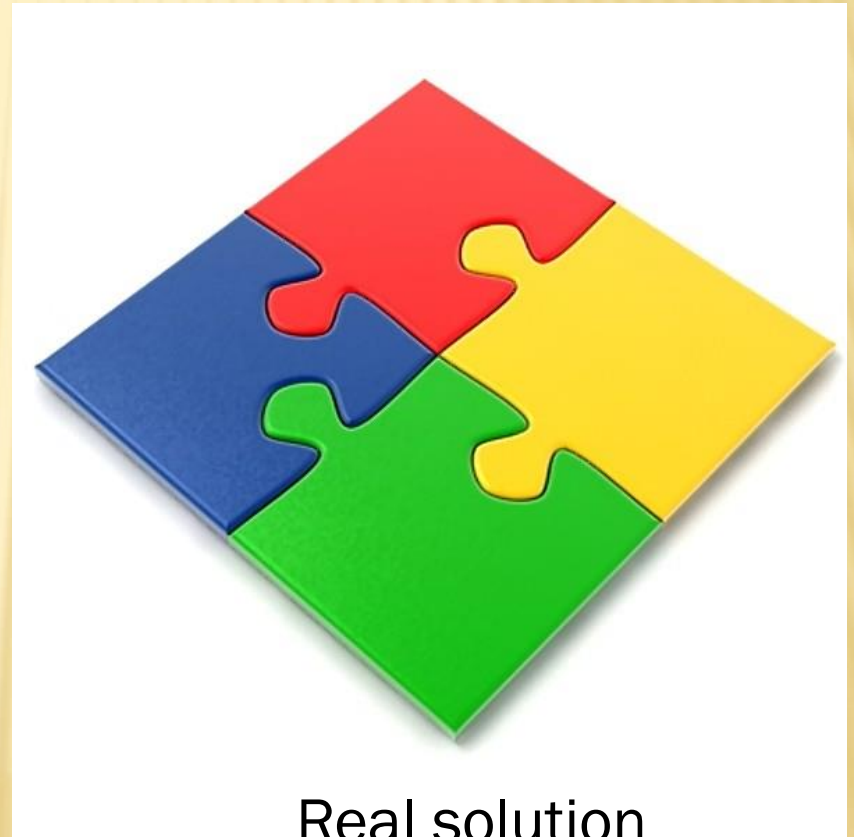
Consider the surface area of puzzle pieces and relate them to the volume of individual components in solutions. The partial molar volume assigned to each component in a real solution is more or less than their volumes at pure state depending on their interactions



Ideal solution

$$nM = \sum n_i V_i$$

$$V_i > \bar{V}_i$$



Real solution

$$nV = \sum n_i \bar{V}_i$$

Although partial properties are shared system properties, in other words they are obtained from the system property, they may be needed in calculation of the total property of another system they become a part of



Partial property of each species in the solution is required in order to obtain the total property of the solution

Partial molar volume \bar{V}_i of a species is a function of its molar ratio x_i

$$x_i = \frac{n_i}{\sum n_i}$$

So both total solution property and individual partial property approach the pure species property as a solution becomes pure in species i:

$$\lim_{x_i \rightarrow 1} M = \lim_{x_i \rightarrow 1} \bar{M}_i = M_i$$

Consider adding a drop of water to a beaker containing an equimolar mixture of alcohol and water at room temperature T and atmospheric pressure P . The drop that is also at T and P , contains Δn_w moles

Allowing enough time for thermal equilibrium, you measure the volume change and see that

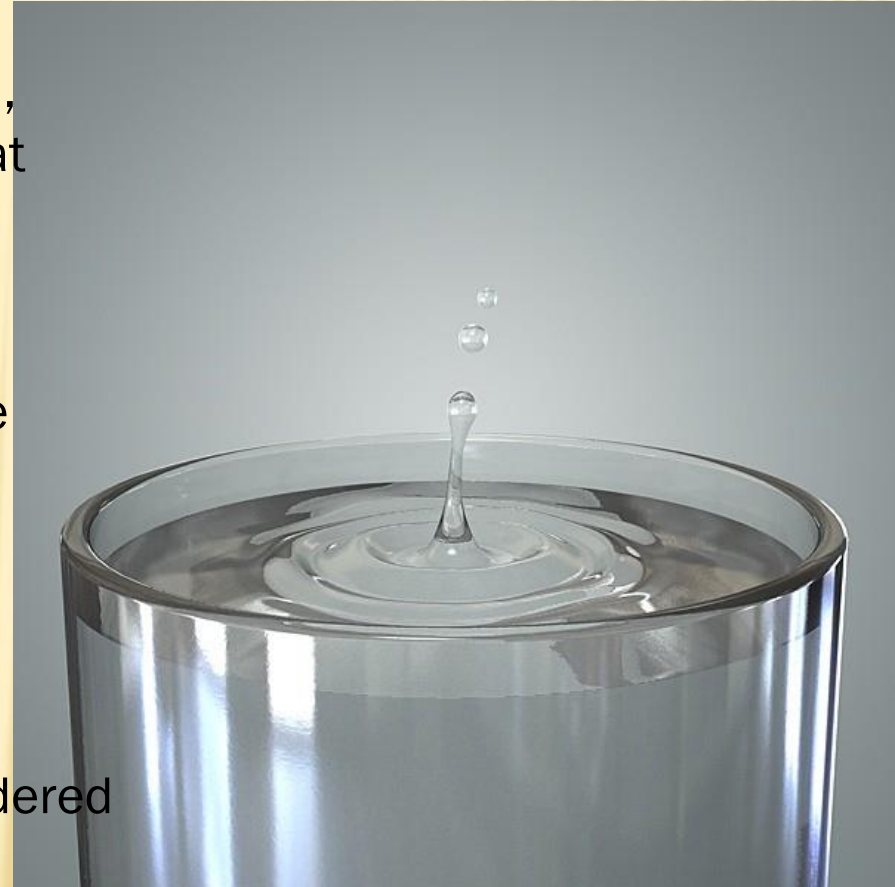
$$\Delta(nV) = \widetilde{V}_w \Delta n_w < V_w \Delta n_w$$

where V_w is the molar volume of pure water and \widetilde{V}_w represents the effective molar volume of water in the solution

$$\widetilde{V}_w = \frac{\Delta(nV)}{\Delta n_w}$$

The effective molar volume of water is considered a property of the original equimolar solution when the process is taken to the limit of an infinitesimal drop

$$\widetilde{V}_w = \lim_{\Delta n_w \rightarrow 0} \frac{\Delta(nV)}{\Delta n_w} = \frac{d(nV)}{dn_w} \quad \text{or} \quad \overline{V}_w = \left(\frac{\partial nV}{\partial n_w} \right)_{T,P,n_a}$$



Hence

$$\bar{V}_i = \left(\frac{\partial nV}{\partial n_i} \right)_{T,P,n_j}$$

Total molar volume of a solution is equal to the sum of the product of the partial molar volume of each species and its mole number

$$nV = n_1\bar{V}_1 + n_2\bar{V}_2 + n_3\bar{V}_3 + \cdots + n_m\bar{V}_m$$

Total differential equation of solution volume:

$$d(nV) = \left[\frac{\partial(nV)}{\partial P} \right]_{T,n} dP + \left[\frac{\partial(nV)}{\partial T} \right]_{P,n} dT + \sum_i \left[\frac{\partial(nV)}{\partial n_i} \right]_{P,T,n_j} dn_i$$

At constant temperature and pressure

$$d(nV) = \sum_i \bar{V}_i dn_i$$

since $n_i = x_i n$,

$$dn_i = x_i dn + n dx_i$$

And since the complete differential of total volume $d(nV) = ndV + Vdn$,

$$ndV + Vdn = \sum_i \bar{V}_i (x_i dn + n dx_i)$$

Separating the terms n and dn ,

$$\left(dV - \sum_i \bar{V}_i dx_i \right) n + \left(V - \sum_i \bar{V}_i x_i \right) dn = 0$$

The solution may contain any moles n , and its size dn may vary by any value

Thus

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

or

$$nV = \sum_i n_i \bar{V}_i$$

Example – How much water must be added to 1000 ml of NiSO_4 -water solution containing 96% $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ by volume in order to make a plating solution containing 64% $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ by volume?

Partial molar volume of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ = 98.1 ml for 96% solution, 96.6 ml for 64% solution

Partial molar volume of H_2O = 14.5 ml for 96% solution, 17.1 ml for 64% solution

For a system of constant total composition of $n=1$, total differential of volume is represented as

$$dV = \left[\frac{\partial V}{\partial P} \right]_{T,n} dP + \left[\frac{\partial V}{\partial T} \right]_{P,n} dT + \sum_i \bar{V}_i dx_i$$

Comparing with the general expression for $dV = \sum_i x_i d\bar{V}_i + \sum_i \bar{V}_i dx_i$ and substitution yields:

$$\left[\frac{\partial V}{\partial P} \right]_{T,n} dP + \left[\frac{\partial V}{\partial T} \right]_{P,n} dT - \sum_i x_i d\bar{V}_i = 0$$

The equation must hold for all changes in P , T , and \bar{V}_i caused by changes of state in a homogeneous phase. For constant T and P ,

$$\sum_i x_i d\bar{V}_i = 0$$

Partial properties of species making up a solution are dependent on each other

So far relationships between total and partial volume of solutions have been discussed

The same relationships hold for other extensive properties including enthalpy, entropy, internal energy and Gibbs free energy

$$V = x_1 \bar{V}_1 + x_2 \bar{V}_2 + \cdots + x_m \bar{V}_m$$

$$dV = dx_1 \bar{V}_1 + dx_2 \bar{V}_2 + \cdots + dx_m \bar{V}_m$$

$$x_1 d\bar{V}_1 + x_2 d\bar{V}_2 + \cdots + x_m d\bar{V}_m = 0$$

$$S = x_1 \bar{S}_1 + x_2 \bar{S}_2 + \cdots + x_m \bar{S}_m$$

$$dS = dx_1 \bar{S}_1 + dx_2 \bar{S}_2 + \cdots + dx_m \bar{S}_m$$

$$x_1 d\bar{S}_1 + x_2 d\bar{S}_2 + \cdots + x_m d\bar{S}_m = 0$$

$$H = x_1 \bar{H}_1 + x_2 \bar{H}_2 + \cdots + x_m \bar{H}_m$$

$$dH = dx_1 \bar{H}_1 + dx_2 \bar{H}_2 + \cdots + dx_m \bar{H}_m$$

$$x_1 d\bar{H}_1 + x_2 d\bar{H}_2 + \cdots + x_m d\bar{H}_m = 0$$

$$G = x_1 \bar{G}_1 + x_2 \bar{G}_2 + \cdots + x_m \bar{G}_m$$

$$dG = dx_1 \bar{G}_1 + dx_2 \bar{G}_2 + \cdots + dx_m \bar{G}_m$$

$$x_1 d\bar{G}_1 + x_2 d\bar{G}_2 + \cdots + x_m d\bar{G}_m = 0$$

$$U = x_1 \bar{U}_1 + x_2 \bar{U}_2 + \cdots + x_m \bar{U}_m$$

$$dU = dx_1 \bar{U}_1 + dx_2 \bar{U}_2 + \cdots + dx_m \bar{U}_m$$

$$x_1 d\bar{U}_1 + x_2 d\bar{U}_2 + \cdots + x_m d\bar{U}_m = 0$$

Partial properties in binary solutions

Equations covered so far enable the calculation of a partial property as a function of composition. An alternative graphical way is more convenient for binary solutions

$$M = x_A \bar{M}_A + x_B \bar{M}_B$$

$$dM = x_A d\bar{M}_A + x_B d\bar{M}_B + \bar{M}_A dx_A + \bar{M}_B dx_B$$

Since $x_A + x_B = 1$, $dx_A = -dx_B$

$$dM = x_A d\bar{M}_A + x_B d\bar{M}_B + (\bar{M}_A - \bar{M}_B) dx_A$$

Partial property changes total to 0

$$\frac{dM}{dx_A} = (\bar{M}_A - \bar{M}_B)$$

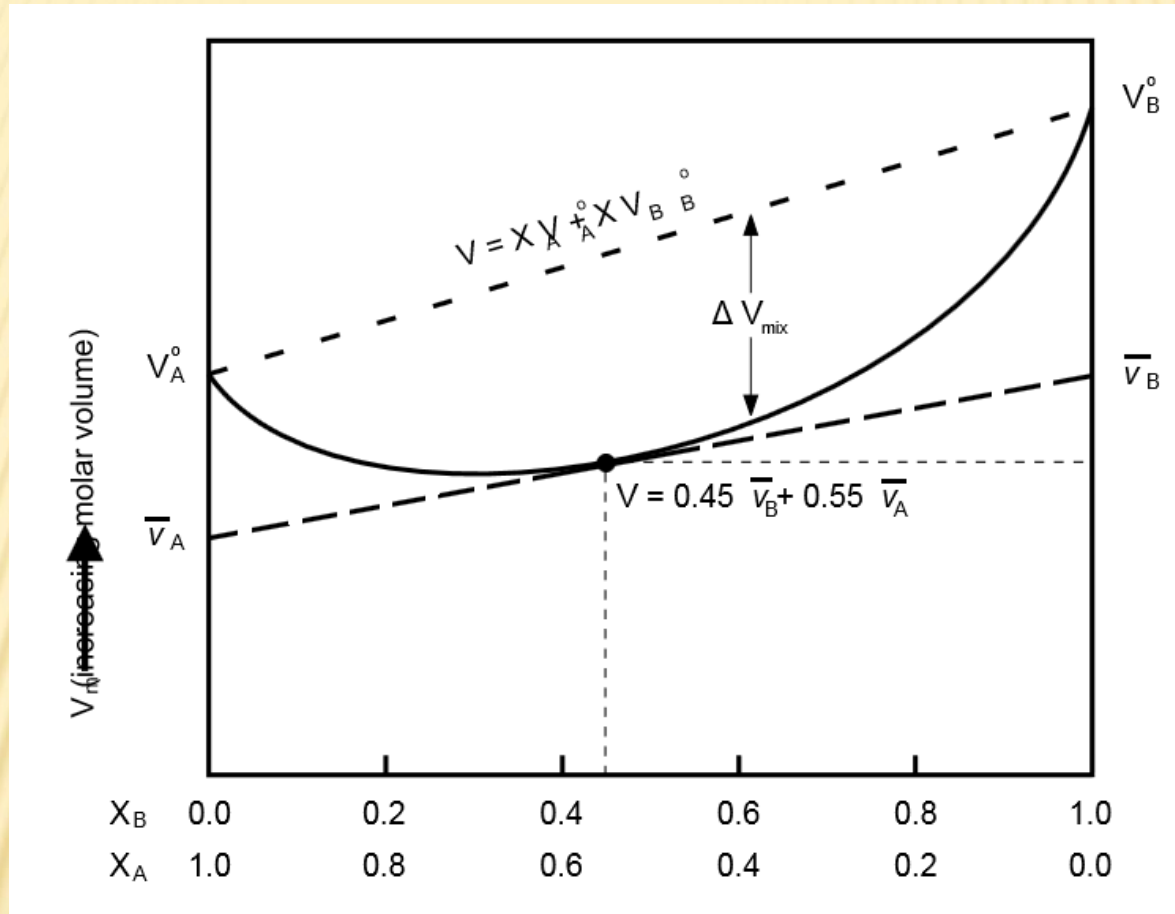
$$M = \bar{M}_A + x_B (\bar{M}_B - \bar{M}_A)$$

$$M = x_A (\bar{M}_A - \bar{M}_B) + \bar{M}_B$$

$$\bar{M}_A = M - x_B \frac{dM}{dx_B}$$

$$\bar{M}_B = M - x_A \frac{dM}{dx_A}$$

The relationships just derived enable determination of partial molar properties of components when the total solution property and its variation with concentration is known



$$\bar{V}_A = V - x_B \frac{dV}{dx_B}$$

$$\bar{V}_B = V - x_A \frac{dV}{dx_A}$$

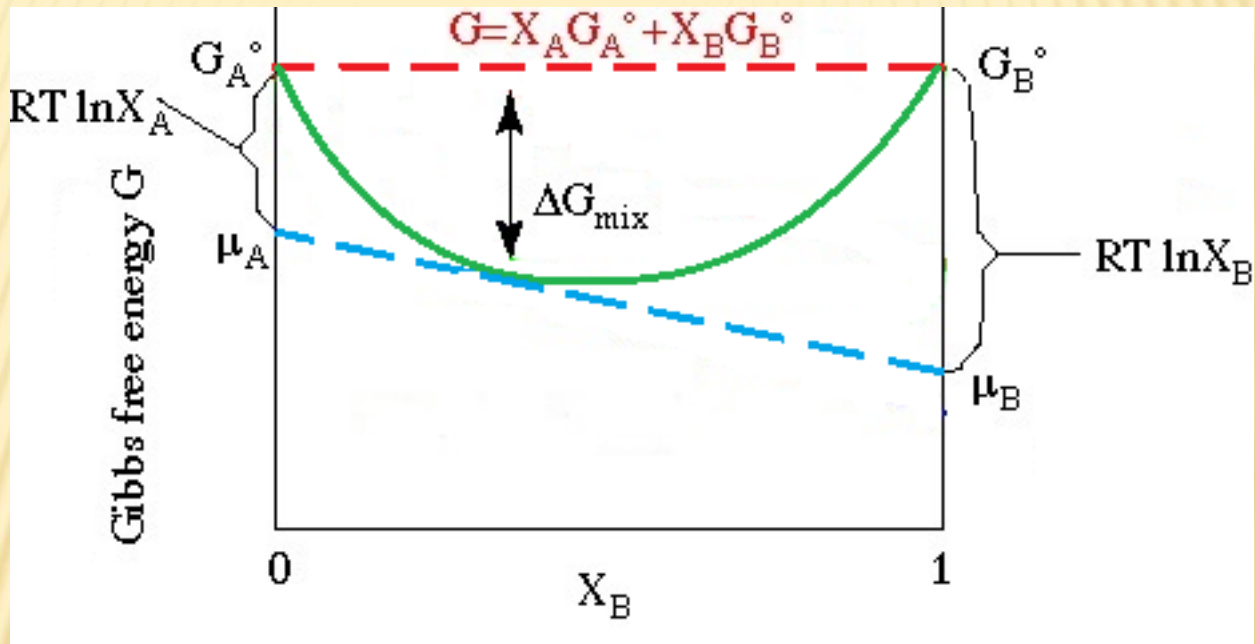
Example - Derive expressions for the partial molar volumes of the components of a binary solution as a function of composition. The total volume change of mixing is

$$\Delta V_M = 2.7x_Ax_B \text{ cm}^3/\text{mol}$$

$$\overline{\Delta V}_A = \Delta V_M - x_B \frac{d\Delta V_M}{dx_B}$$

$$\overline{\Delta V}_B = \Delta V_M - x_A \frac{d\Delta V_M}{dx_A}$$

The relationships just derived enable determination of partial molar properties of components when the total solution property and its variation with concentration is known

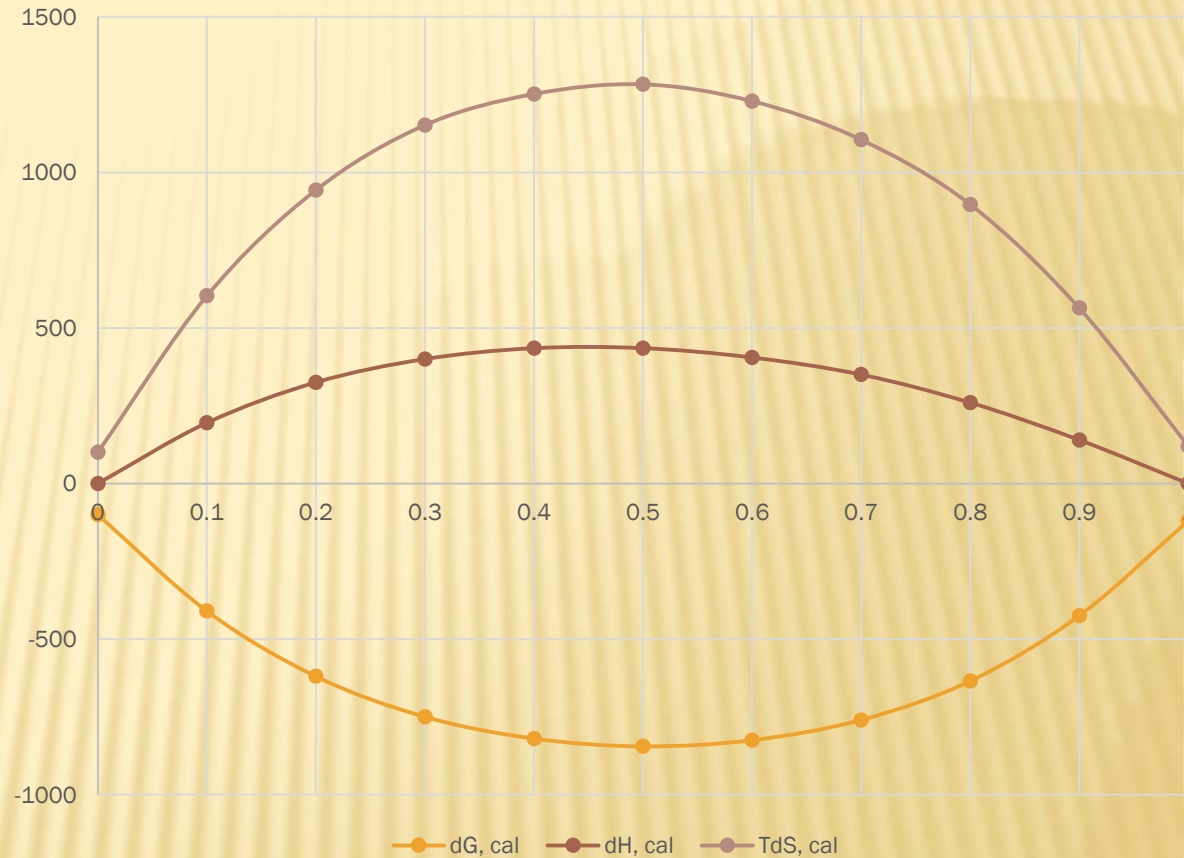


$$\bar{G}_A = \mu_A = G x_B - \frac{dG}{dx_B}$$

Recall that $\mu_A^{id} = G_A^0 + RT \ln x_A$

Example – Variation of total molar properties of the Cd-Sn alloy system with composition at 773 K are given in table form. Obtain the partial molar properties of the components graphically for 45% Sn and calculate the activities of the components at 773 K

X Sn	dG, cal	dH, cal	TdS, cal
0	-100	0	100
0.1	-410	195	603
0.2	-620	325	943
0.3	-750	400	1152
0.4	-820	435	1252
0.5	-845	435	1283
0.6	-825	405	1229
0.7	-760	350	1105
0.8	-635	260	897
0.9	-425	140	564
1	-120	0	120



$$G_{Sn} = G_{Sn}^0 + RT \ln a_{Sn}$$

Relationships between partial molar properties

The sound basis of thermodynamic relationships among pure substances with constant composition allows us to make use of all of them for analysis of solutions with variable composition by substituting molar properties of pure substances with the partial molar properties

$$\Delta \bar{G}_i = \Delta \bar{H}_i - T \Delta \bar{S}_i$$

$$\left(\frac{\partial \bar{G}_i}{\partial T} \right)_{P, n_j} = -\bar{S}_i$$

$$\left[\frac{\partial (\bar{G}_i/T)}{\partial (1/T)} \right]_{P, n_j} = \bar{H}_i$$

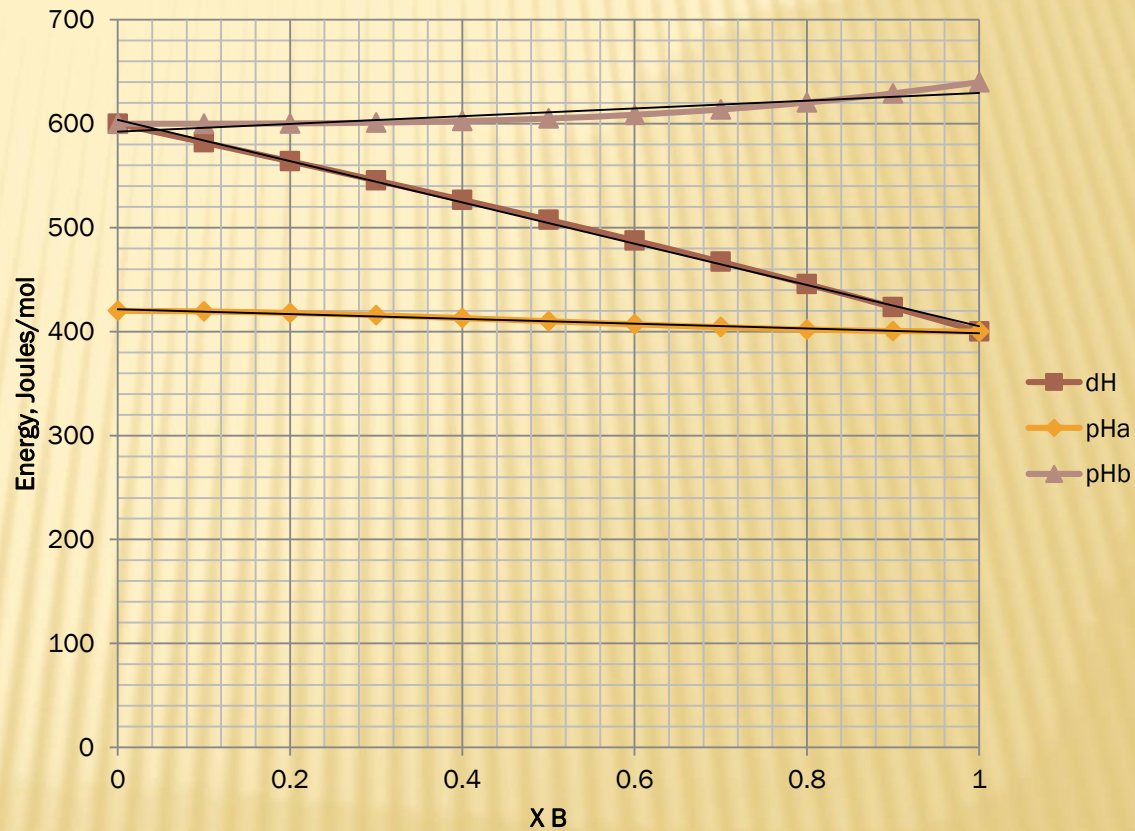
$$\left(\frac{\partial \bar{G}_i}{\partial P} \right)_{T, n_j} = \bar{V}_i$$

$$d\bar{U} = Td\bar{S} - Pd\bar{V} \quad d\bar{G} = \bar{V}dP - \bar{S}dT \quad d\bar{H} = Td\bar{S} + \bar{V}dP \quad d\bar{A} = -Pd\bar{V} - \bar{S}dT$$

Example – Determine expressions for partial molar enthalpies and the pure species enthalpies for an arbitrary binary solution system of A and B. The total molar enthalpy variation by concentration is given as:

$$H = 400x_A + 600x_B + x_Ax_B(40x_A + 20x_B) \text{ J/mol}$$

$$\overline{M}_A = M - x_B \frac{dM}{dx_B}$$



Example – The free energy of a binary ideal solution of species 1 and 2 at ambient T and P is represented by the equation

$$G^{id} = x_1 G_1 + x_2 G_2 + RT(x_1 \ln x_1 + x_2 \ln x_2) \text{ J/mole}$$

Determine expressions for \bar{G}_1 and \bar{G}_2 at equimolar concentration

$$\bar{G}_1 = G - x_2 \frac{dG}{dx_2}$$
$$\bar{G}_2 = G - x_1 \frac{dG}{dx_1}$$

Obtaining total solution property from one of the components'

Total solution property in terms of partial properties is simplified by virtue of the equation $X_A + X_B = 1$

$$M = x_A \bar{M}_A + x_B \bar{M}_B$$

$$\bar{M}_A = M + (1 - X_A) \left(\frac{dM}{dX_A} \right)$$

Multiplying both sides by dX_A and dividing by X_B^2

$$\frac{\bar{M}_A dX_A}{X_B^2} = \frac{M dX_A + (1 - X_A) dM}{X_B^2}$$

Replacing $(1 - X_A) = X_B$ and $dX_A = -dX_B$

$$\frac{\bar{M}_A dX_A}{X_B^2} = \frac{-M dX_B + X_B dM}{X_B^2} = d \left(\frac{M}{X_B} \right)$$

Integrating both sides gives

$$\int_{\frac{M}{X_B}(\text{at } X_B=1)}^{\frac{M}{X_B}} d\left(\frac{M}{X_B}\right) = \int_{X_A=0}^{X_A} \frac{\overline{M}_A dX_A}{X_B^2}$$

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

Setting partial mixing or excess properties ΔM^M and M^E equal to zero at $X_B=1$

$$\frac{\Delta M^M}{X_B} = \int_{X_A=0}^{X_A} \frac{\Delta \overline{M}_A^M dX_A}{X_B^2}$$

↑
constant

$$\frac{M^E}{X_B} = \int_{X_A=0}^{X_A} \frac{\overline{M}_A^E dX_A}{X_B^2}$$

↑
constant

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

Values of integrals can be obtained either analytically or graphically

The following steps are involved in analytical integration:

- Replacement of the property \overline{M}_A , $\Delta\overline{M}_A^M$ or $\Delta\overline{M}_A^E$ into the integral
- Organization of the function inside the integral in such a way to leave only one variable
- Integration and replacement of the limits

Graphical integration involves determination of the area under the curve \overline{M}_A/X_B^2 , $\Delta\overline{M}_A^M/X_B^2$ or $\Delta\overline{M}_A^E/X_B^2$ vs. X_A between the limits

Example - Partial volume of mixing of A is given as $\overline{\Delta V}_A = 10x_B^2 + 40x_B^3$
Find the total volume of the solution at $x_A = 0.669$

$$\frac{\Delta V}{X_B} = \int_{X_A=0}^{X_A=0.669} \frac{\overline{\Delta V}_A dX_A}{X_B^2} = \int_{X_A=0}^{X_A=0.669} \frac{(10x_B^2 + 40x_B^3) dX_A}{X_B^2}$$

$$\frac{\Delta V}{0.331} = \int_{X_A=0}^{X_A=0.669} (10 + 40x_B) dX_A = \int_{X_A=0}^{X_A=0.669} (50 - 40X_A) dX_A$$

$$\frac{\Delta V}{0.331} = 50(0.669) - 20(0.669)(0.669) = 24.5$$

$$\Delta V = 8.11 \text{ cm}^3$$

To check the solution, $\Delta V = x_A x_B (30x_A + 50x_B)$

$$\Delta V = (0.669)(0.331)(30(0.669) + 50(0.331)) = 8.11 \text{ cm}^3$$



Homework question – The activity of a component for binary systems comprised of species that are chemically similar is represented as $\ln \alpha_1 = 1.7613(1-2x_1)$
Obtain G/RT value for $x_1 = 0.398$

$$\frac{G}{RT(X_2)} = \int_{X_1=0}^{X_1=0.398} \frac{\overline{G}_1 dX_1}{RTX_2^2}$$



Further derivation of the fundamental partial property equations enable determination of the partial property of one component, \bar{M}_A if the variation of the other's, \bar{M}_B as a function of composition is known

$$x_A d\bar{M}_A + x_B d\bar{M}_B = 0$$

substituting by $x_A = 1 - x_B$ yields

$$d\bar{M}_B = - \left(\frac{1 - x_B}{x_B} \right) d\bar{M}_A$$

Equation can be integrated between limits \bar{M}_B and M_B^o

$$\int_{M_B^o}^{\bar{M}_B} d\bar{M}_B = \bar{M}_B - M_B^o = \int_{(\bar{M}_A)_{x_B=1}}^{(\bar{M}_A)_{x_B=x}} \left(\frac{1 - x_B}{x_B} \right) d\bar{M}_A$$

Because \bar{M}_B is constant at $x_B = 1$ and equals M_B^o as $\left(\frac{1-x_B}{x_B} \right)$ equals 0

\bar{M}_B is obtained from the integration by adding M_B^o directly if $\bar{M}_A = f(x_B)$ is known

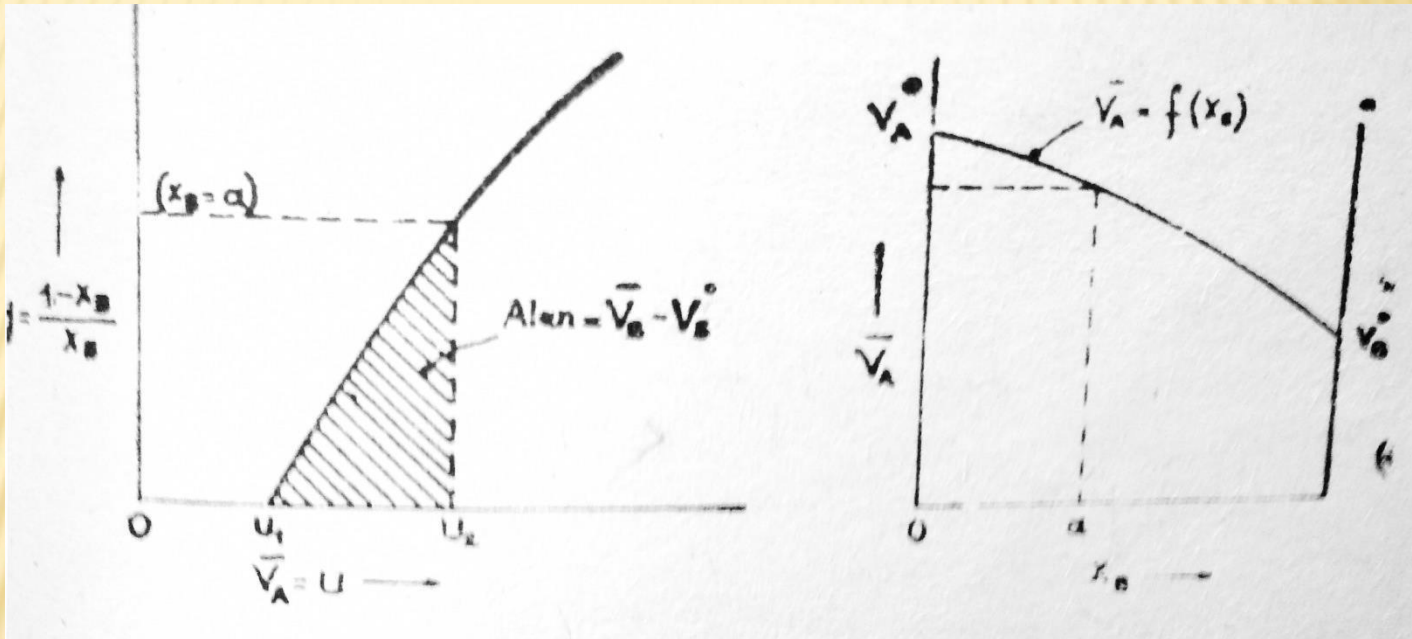
$$\bar{M}_B - M_B^o = - \int_{(\bar{M}_A)_{XB=1}}^{(\bar{M}_A)_{XB=x}} \left(\frac{1 - x_B}{x_B} \right) d\bar{M}_A$$

Analytical determination involves the following steps:

- Organize \bar{M}_A as a function of only one composition variable
- Take the derivative of \bar{M}_A and replace it into the integral
- Organize the function inside the integral in such a way to leave only one variable and change the limits of the integral if necessary, to make it in accord with the derivative of the integral. Make use of the relationship $dX_A = -dX_B$
- Integrate the function, replace the limits to determine the value of the integral

Graphical determination of $\bar{M}_B - M_B^0$ is possible by plotting a $\left(\frac{x_A}{x_B}\right) - \bar{M}_A$ graph

The area under the curve between the limits $(\bar{V}_A)_{XB=1}$ and $(\bar{V}_A)_{XB=a}$ gives $\bar{V}_B - V_B^0$



$$\bar{V}_B - V_B^0 = \int_{(\bar{V}_A)_{XB=1}}^{(\bar{V}_A)_{XB=a}} \left(\frac{x_A}{x_B}\right) d\bar{V}_A$$

$$\bar{V}_B - V_B^0 = \int_{U_1}^{U_2} y dU$$

However there are some limitations with graphical determination:

- The value of \overline{M}_A becomes $-\infty$ if \overline{M}_A has logarithmic composition terms
- X_A/X_B becomes ∞ when X_B becomes zero

These problems may be resolved for excess properties and properties of mixing using the α -function:

For any component i , α_i is defined as

$$\alpha_i = \frac{\overline{M}_i^E}{(1 - X_i)^2}$$

α -function = 0/0 when X_i becomes 1 so that its integral gives a finite value

Derivation of the α -function

$$\overline{M}_B^E \text{ at } X_B = - \int_{(\overline{M}_A^E)_{XB=1}}^{(\overline{M}_A^E)_{XB=a}} \left(\frac{X_A}{X_B} \right) d\overline{M}_A^E$$

$$\text{Let } \overline{M}_A^E = \alpha_A X_B^2,$$

$$\text{Then } d\overline{M}_A^E = d\alpha_A X_B^2 + 2\alpha_A X_B dX_B$$

Replacing into integral yields

$$\overline{M}_B^E \text{ at } X_B = - \int_{(\alpha_A)_{XB=1}}^{(\alpha_A)_{XB=a}} \left(\frac{X_A}{X_B} \right) X_B^2 d\alpha_A - \int_{XB=1}^{XB=a} \left(\frac{X_A}{X_B} \right) 2\alpha_A X_B dX_B$$

$$\overline{M}_B^E \text{ at } X_B = - \int_{(\alpha_A)_{XB=1}}^{(\alpha_A)_{XB=a}} X_A X_B d\alpha_A - \int_{XB=1}^{XB=a} 2\alpha_A X_A dX_B$$

The first integral is expanded by virtue of the identity $\int d(xy) = \int ydx + \int xdy$

$$\int_{(\alpha_A)_{XB=1}}^{(\alpha_A)_{XB=a}} X_A X_B d\alpha_A = \int d(X_A X_B \alpha_A) - \int \alpha_A d(X_A X_B)$$

$$\overline{M}_B^E \text{ at } X_B = - \int d(X_A X_B \alpha_A) + \int \alpha_A d(X_A X_B) - \int 2\alpha_A X_A dX_B$$

$$\overline{M}_B^E \text{ at } X_B = -X_A X_B \alpha_A + \int \alpha_A X_A dX_B + \int \alpha_A X_B dX_A - \int 2\alpha_A X_A dX_B$$

Grouping the last terms,

$$\overline{M}_B^E \text{ at } X_B = -X_A X_B \alpha_A - \int \alpha_A (2X_A - X_A + X_B) dX_B$$

$$\overline{M}_B^E \text{ at } X_B = -X_A X_B \alpha_A - \int \alpha_A dX_B$$

$$\alpha_A = \frac{\overline{M}_A^E}{X_B^2}$$

Numerical value for $-X_A X_B \alpha_A$ is readily calculated, the value of the integral can be determined graphically or analytically

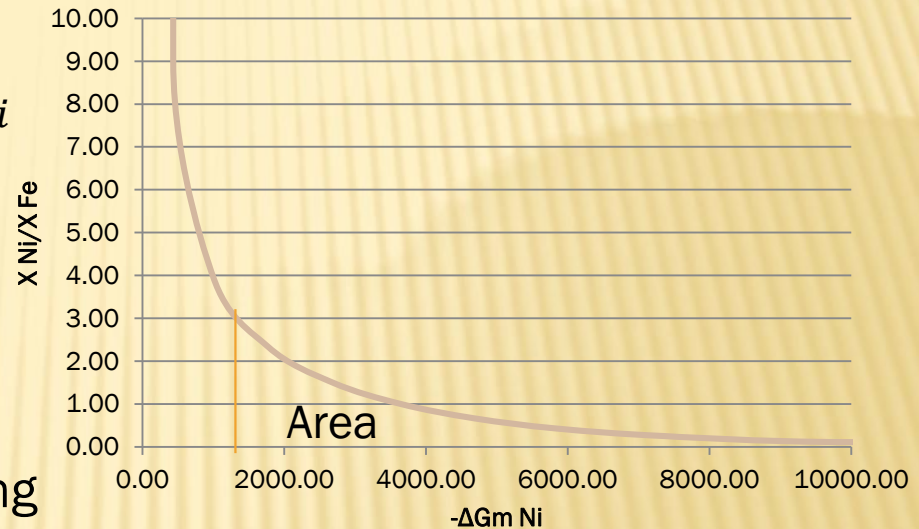
Analytical integration with α -function is done by replacing α_A into the equation and integrating between the limits

Graphical determination is done by obtaining the area under X_B vs. α_A graph

Example – Consider the binary system Fe-Ni at 1600 °C

X Ni	1.00	0.90	0.80	0.70	0.60	0.50	0.40	0.30	0.20	0.10	0.00
a Ni	1.00	0.89	0.77	0.62	0.49	0.37	0.28	0.21	0.14	0.07	0.00
ΔG_m Ni	0.00	-432.00	-989.00	-1773.00	-2684.00	-3647.00	-4681.00	-5841.00	-7399.00	-10024.00	$-\infty$
X Ni/X Fe	∞	9.00	4.00	2.33	1.50	1.00	0.67	0.43	0.25	0.11	0.00

$$\overline{\Delta M}_{Fe} = - \int_{(\overline{\Delta M}_{Ni})_{X_{Fe}=1}}^{(\overline{\Delta M}_{Ni})_{X_{Fe}=a}} \left(\frac{1 - x_{Fe}}{x_{Fe}} \right) d\overline{\Delta M}_{Ni}$$



The value of partial Gibbs energy of mixing goes to infinity at the lower limit and results in an unbounded area

This problem is overcome by using partial excess Gibbs energy which reaches a finite value of $RT \ln \gamma_{Ni}^0$ at $X_{Ni} = 0$

Using partial excess values provides good results as long as $X_{Fe} > 0$ since $X_{Ni}/X_{Fe} = \infty$ at $X_{Fe} = 0$

α -function enables obtaining finite integral over all X values

