Lecture 21

Thermodynamics of Solutions

Tutorial - Problem Solving

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6.15 The molar heat of formation of liquid brass according to the reaction

$$(1-X)\ \{Cu\} + X\ \{Zn\} = \{Cu\text{-}Zn\}$$

is given by $\Delta H^M = -29700\ X\ (1-X)$ joules, where X is the atom fraction of zinc. Determine the expressions relating the partial molar heats of formation of copper and zinc in liquid brass to the alloy composition.

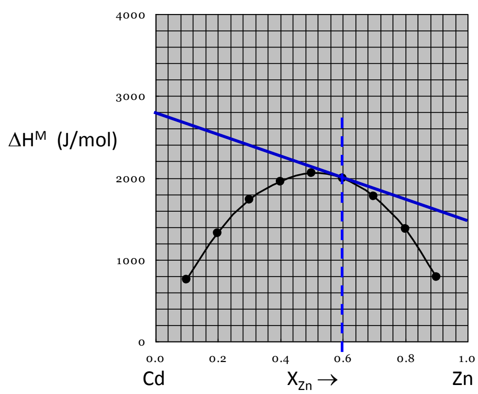
6.18 The activity coefficient of Zn in liquid Cd-Zn alloys at 435 C can be represented by

$$\ln \gamma_{Zn} = 0.87\ X_{Cd}^2 - 0.30\ X_{Cd}^3$$

Derive the corresponding expression for the composition dependence of $\ln \gamma_{Cd}$, and hence calculate a_{Cd} in the $X_{Cd} = 0.3$ alloy at 435 C.

6.19 Given the integral heats of mixing (ΔH^M, J/mol) of zinc with its mole fraction (X_{Zn}) in a Zn-Cd alloy calculate the partial molar heats of mixing of zinc and cadmium, containing 0.6 atom fraction zinc at 700 C.

X_{Zn}	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
ΔH^M	753	1326	1728	1958	2054	2000	1774	1377	787



$\Delta \underline{H}^M_{Cd}$ = 2800 J/mol

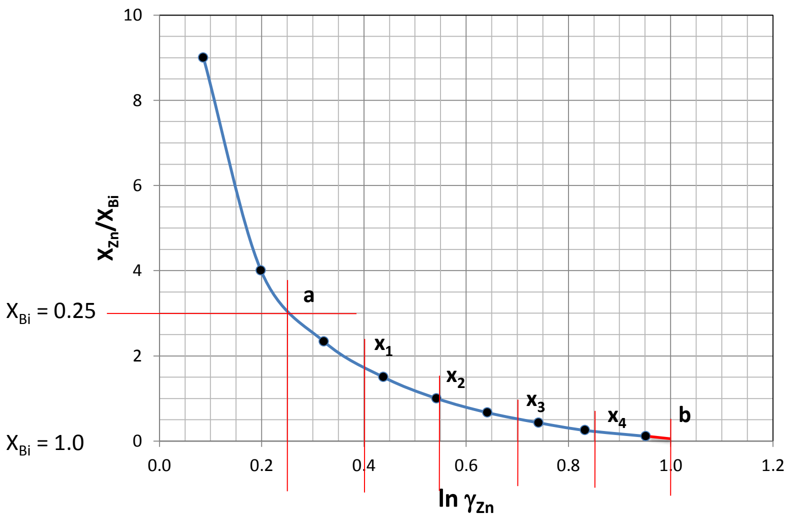
$\Delta \underline{H}^M_{Zn}$ = 1500 J/mol

6.21 Calculate the activity of bismuth in a Bi-Zn alloy containing 75 atom% Zn at 600 C from the following data:

X_{Zn}	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
γ_{Zn}	2.591	2.303	2.098	1.898	1.721	1.551	1.384	1.219	1.089

$$\ln \gamma_{Bi} = -\int_{X_{Bi}=1}^{X_{Bi}=0.25} \left(\frac{X_{Zn}}{X_{Bi}}\right) d \ln \gamma_{Zn} = +\int_{X_{Bi}=0.25}^{X_{Bi}=1} \left(\frac{X_{Zn}}{X_{Bi}}\right) d \ln \gamma_{Zn}$$

X_{Zn}	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
γ_{Zn}	2.591	2.303	2.098	1.898	1.721	1.551	1.384	1.219	1.089
X_{Bi}	0.9	0.8	0.7	0.6	0.5	0.4	0.3	0.2	0.1
$\ln \gamma_{Zn}$	0.95	0.83	0.74	0.64	0.54	0.44	0.32	0.2	0.09
X_{Zn}/X_{Bi}	0.11	0.25	0.43	0.67	1.00	1.50	2.33	4.00	9.00



$a = 0.25$, $b = 1.00$
$n = 5$
$h = (b-a)/n = 0.15$

$f(a) = 3.0$ $\quad f(x_1) = 1.75$ $\quad f(x_2) = 1.0$

$(f(x_3) = 0.5$ $\quad f(x_4) = 0.25$ $\quad f(b) = 0.0$

$$S = h\left(\frac{f(a) + f(b)}{2} + f(x_1) + f(x) + \ldots\ldots + f(x_{n-1})\right)$$

$$= \mathbf{0.15}\left(\mathbf{(3.0+0)/2 + 1.75 + 1.0 + 0.5 + 0.25}\right)$$

$$= \mathbf{0.75}$$

$\ln \gamma_{Bi} = 0.75$

$\gamma_{Bi} = 2.12$

$a_{Bi} = \gamma_{Bi} \cdot X_{Bi}$

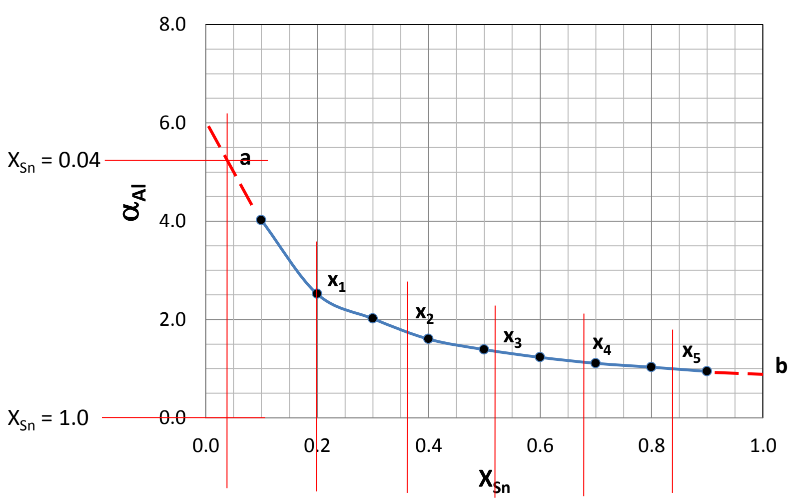
$= 1.78\,(0.25) = 0.53$

6.22 Calculate the activity of tin in an Al-Sn alloy containing 4 atom% Sn at 723 C from the following data:

X_{Al}	0.9	0.8	0.7	0.6	0.5	0.4	0.3	0.2	0.1
γ_{Al}	1.041	1.106	1.199	1.292	1.415	1.557	1.722	1.933	2.148

$$\ln \gamma_{Sn} = - X_{Sn} X_{Al} \alpha_{Al} + \int_{X_{Sn}=0.04}^{X_{Sn}=1.0} \alpha_{Al} \, dX_{Sn} \qquad \alpha_{Al} = \frac{\ln \gamma_{Al}}{X_{Sn}^2}$$

X_{Al}	0.9	0.8	0.7	0.6	0.5	0.4	0.3	0.2	0.1
γ_{Al}	1.041	1.106	1.199	1.292	1.415	1.557	1.722	1.933	2.148
X_{Sn}	0.9	0.8	0.7	0.6	0.5	0.4	0.3	0.2	0.1
α_{Al}	4.02	2.52	2.02	1.6	1.39	1.23	1.11	1.03	0.94



a = 0.04, b = 1.00
n = 6
h = (b-a)/n = 0.16

f(a) = 5.25 f(x_1) = 2.50 f(x_2) = 1.75
(f(x_3) = 1.45 f(x_4) = 1.20 f(x_4) = 1.00 f(b) = 0.90

$$S = h\left(\frac{f(a) + f(b)}{2} + f(x_1) + f(x) + \ldots\ldots + f(x_{n-1})\right)$$

$$= 0.16\left((5.25+0.90)/2 + 2.50 + 1.75 + 1.45 + 1.20 + 1.00\right)$$

$$= 1.76$$

$$\ln \gamma_{Sn} = -X_{Sn} X_{Al} \alpha_{Al} + \int_{X_{Sn}=0.04}^{X_{Sn}=1.0} \alpha_{Al}\, dX_{Sn}$$

$$= -(0.04)(0.96)(5.25) + 1.76 = 1.56$$

$$\gamma_{Sn} = 4.75$$

$$a_{Sn} = \gamma_{Sn} \cdot X_{Sn}$$

$$= 4.75\,(0.04) = 0.19$$

6.26 Estimate the activity coefficient of sulphur in a metallic bath containing 0.05 wt% sulphur, 1.2 wt% silicon, 4.0 wt% carbon, and 1.8 wt% manganese, given that $e_S^S = -0.028$, $e_S^{Si} = 0.065$, $e_S^C = 0.24$, and $e_S^{Mn} = -0.02$.

$$\log f_S = \log f_S^S + \log f_S^{Si} + \log f_S^C + \log f_S^{Mn}$$

$$= e_S^S \cdot \text{wt.\% S} + e_S^{Si} \cdot \text{wt.\% Si} + e_S^C \cdot \text{wt.\% C} + e_S^{Mn} \cdot \text{wt.\% Mn}$$

$$= (-0.028)\,0.05 + (0.065)\,1.20 + (0.24)\,4.0 + (-0.02)\,1.80$$

$$= 1.0$$

$$f_S = 10.01$$

Next Class

Lecture 22

Thermodynamics of Phase Diagrams

Introduction to the Phase Diagrams