a) The Liquid A-B mixture is NOT ideal since $\Delta H_{mix} \neq 0$

b) For the liquid :
$$\begin{cases} \mu_A^\ell = \mu_A^{o\ell} + RT \ln a_A \\ \\ \mu_B^\ell = \mu_B^{o\ell} + RT \ln a_B \end{cases}$$

For the gas phase :
$$\begin{cases} \mu_A^g = \mu_A^{og} + RT \ln P_A \\ \\ \mu_B^g = \mu_B^{og} + RT \ln P_B \end{cases}$$

* When we have pure A, then $a_A = 1$ $P_A = P_A^o$ = vapor pressure above pure A

$$\mu_A^\ell = \mu_A^{o\ell} = \mu_A^{og} + RT \ln P_A^o$$

or
$$\boxed{RT \ln P_A^o = \mu_A^{o\ell} - \mu_A^{og}}$$

Similarly for B :
$$\boxed{RT \ln P_B^o = \mu_B^{o\ell} - \mu_B^{og}}$$

* When $x_B = 0.95$, then

$$\mu_A^\ell = \mu_A^{o\ell} + RT \ln a_A = \mu_A^{og} + RT \ln P_A$$

$$RT \ln a_A = -\underbrace{(\mu_A^{o\ell} - \mu_A^{og})}_{-RT \ln P_A^o} + RT \ln P_A$$

$$\boxed{RT \ln a_A = RT \ln \left(P_A / P_A^o \right)}$$

PROBLEM 1   CONTINUED

similarly for B

$$RT \ln a_B = RT \ln \left(P_B / P_B^\circ \right)$$

$RT \ln a_A$ and $RT \ln a_B$ can be read off of the plot for ΔG_{mix} using the intercept rule.

$\mu_B - \mu_B^\circ = RT \ln a_B$

$\mu_A - \mu_A^\circ = RT \ln a_A$
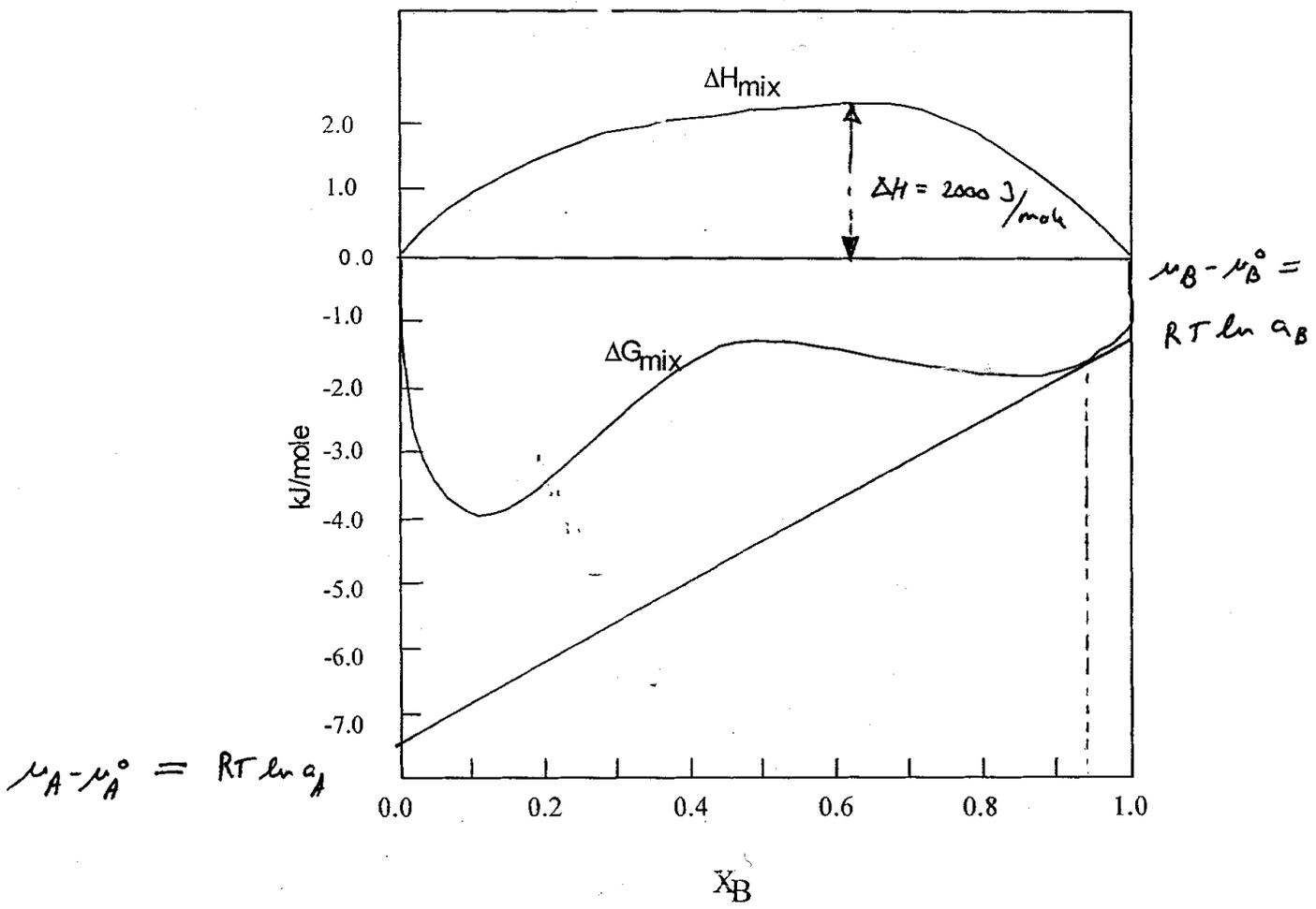
From the plot, we can estimate $a_A = 0.41$ and $a_B = 0.83$

$$P_A = a_A P_A^\circ = 4.1 \times 10^{-6} \text{ atm}$$

$$P_B = a_B P_B^\circ = 8.3 \times 10^{-3} \text{ atm}$$

PROBLEM 1   CONTINUED

c)   total # of moles of mixture : $N_A + N_B = 2.5$ moles

   $X_A = 0.4$

   $X_B = 0.6$

   at $X_B = 0.6$ $\Delta \underline{H}_{mix} \approx 2000$ J/mole   (see figure)

   $\Delta H_{mix} > 0$,   so   mixing will draw heat from the environment

   amount of heat sucked in :

$$Q = \underset{N_{tot}}{\underbrace{2.5}} (2000) = 5000 \text{ J}$$

PROBLEM 2   (LEVEL 1)

microscopic mechanisms that contribute to the increase in entropy of Ferro magnetic Fe-75% Ni as T is increased:

(i) magnetic disordering of the magnetic moments

(ii) configurational disordering of the Ni and Fe atoms

(iii) entropy arising from lattice vibrations

PROBLEM 3 (LEVEL 1)

Si and Ge form ideal solutions in both liquid and solid state.

⟹ phase diagram at high T is a lens diagram

liquid

1414°C

938°C

solid

Si
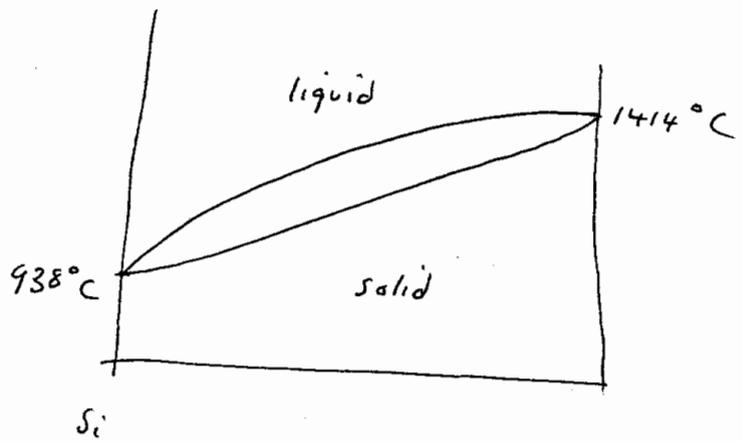
when Ge is added to Si, the melting point of the solution will therefore be higher than 938°C

Problem 4 (Level 1)

concentration

A   x*   B

Gibbs free energy

ΔG_{mix}

solid

liquid
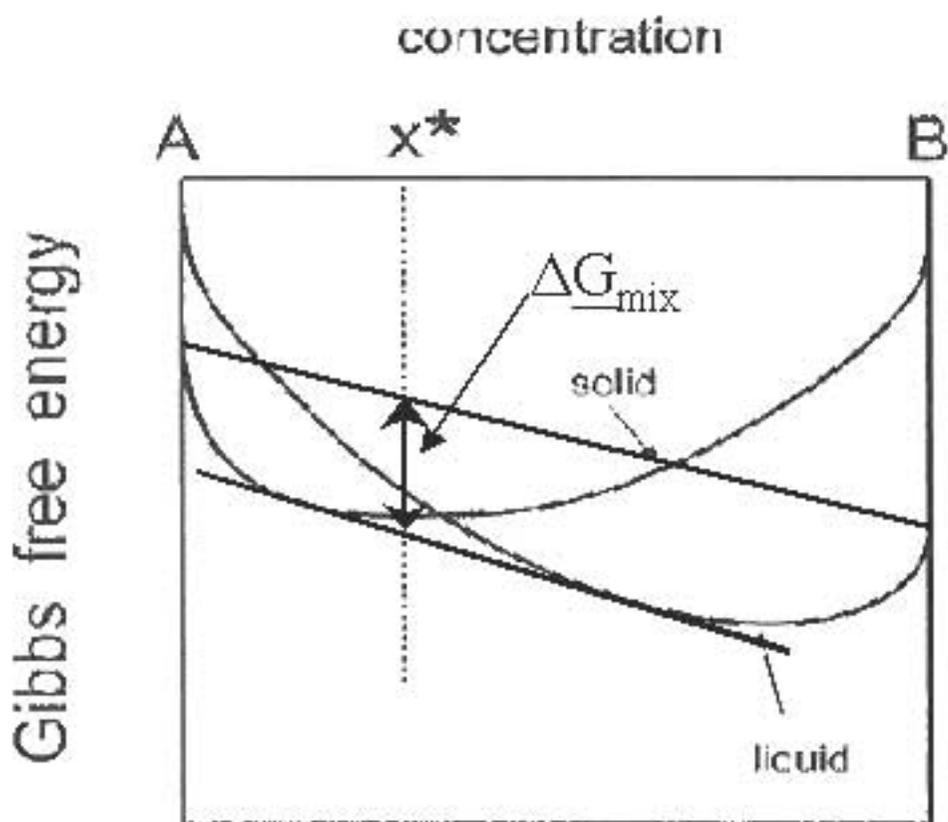
PROBLEM 1   (LEVEL 2)

Cu & Au can form a ~~solid~~ solid solution at high T

or an ordered compound at low T   .

a) * mix ~~are~~ 1 mole of Cu and 1 mol of Au

at 1150° k

* assume ideal solution

$$\Rightarrow \quad \boxed{\Delta \underline{G}_{mix} = RT\left[x \ln x + (1-x) \ln x\right]}$$

where x is the Au concentration and is = 0.5

$$\Delta \underline{S}_{mix} = -6627 \quad J/mol \qquad at \qquad T = 1150° k$$

* Since 1 mole of Cu and 1 mole of Au

$$\Rightarrow \quad 2 \text{ moles of mixture}$$

$$\boxed{\Delta G = 2 \times \Delta \underline{G}_{mix} = -13\,254 \; J}$$

b) For ordered compound,

$$\Delta G_{Cu_{0.5} Au_{0.5}} = \Delta H_{Cu_{0.5} Au_{0.5}} \qquad \left(since \quad \Delta S_{Cu\,Au} = 0\right)$$

$$\boxed{\Delta G_{Cu_{0.5} Au_{0.5}} = -\frac{11904}{2} \; J/mol}$$

at the (first-order) order-disorder transition,

$$\boxed{\Delta G_{Cu_{0.5} Au_{0.5}} = \Delta \underline{G}_{mix}}$$

This occurs at $\boxed{T = 1033 \; k}$

PROBLEM 1 (LEVEL 2)   CONTINUED

c) In ΔG_{mix} for the solid solution, we neglected

$\Delta H_{\underline{mix}}$. Since this system has ordering tendencies,

$\Delta H_{\underline{mix}} < 0$. ~~This will depend~~ Inclusion of a negative $\Delta H_{\underline{mix}}$

~~that~~ in part (b) will decrease the calculated transition

temperature.

PROBLEM 2

The ideal solution entropy formula is a better approximation

at high temperature.

For the ideal solution entropy formula, it is assumed

that every arrangement of A and B atoms are equally

probable. In reality, this is not true since the probability

of an arrangement ν is

$$ P_\nu \sim exp\left(\frac{-E_\nu}{kT}\right) $$

Since different arrangements ν and η typically have

different energies,

$$ \Rightarrow \frac{P_\nu}{P_\eta} = exp\left(\frac{-(E_\nu - E_\eta)}{kT}\right) \neq 1 $$

This ratio does, however, approach 1 as T is increased.

PROBLEM 3   (LEVEL 2)
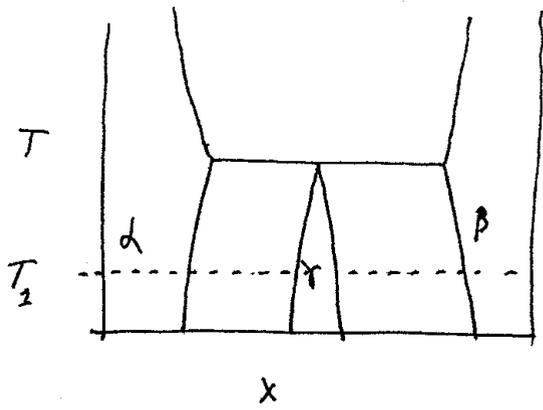
Free energies at T_1
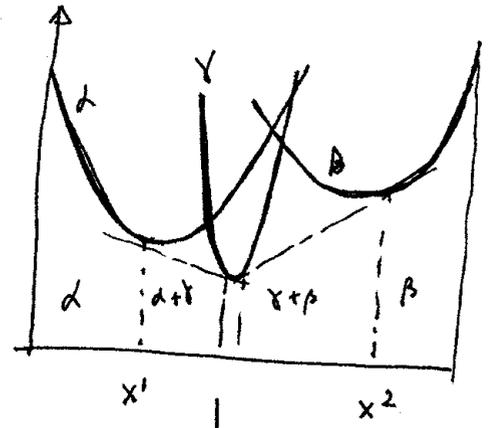
Suppression of the γ-phase yields
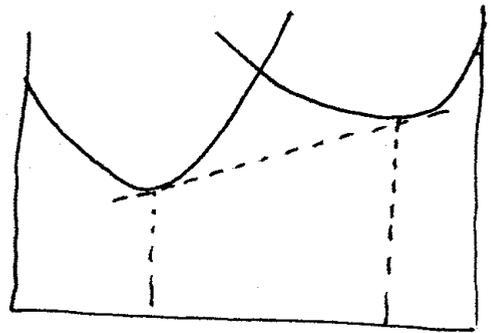
meta stable

phase diagram
(with γ suppressed)
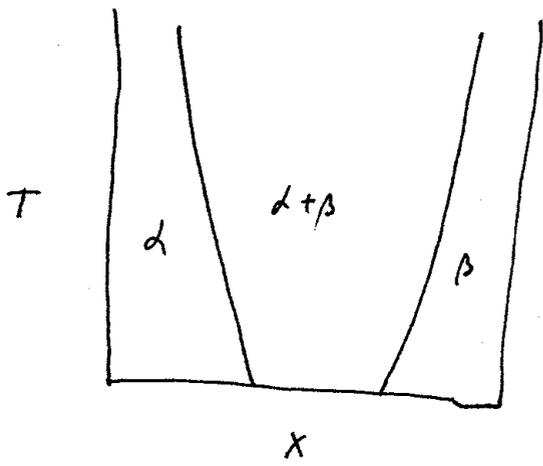
PROBLEM 4 (LEVEL 2)

REGULAR SOLUTION MODEL

$$\Delta \underline{G}_{mix} = Z \omega X_A X_B + RT\left[X_A \ln X_A + X_B \ln X_B\right]$$

with $\omega = \omega_{AB} - \frac{1}{2}(\omega_{AA} + \omega_{BB})$

$\omega = 630 \ J/mol$

$z = 8$

a) (i) $\Delta \underline{H}_{mix} = Z\omega X_A X_B$

(ii) $\Delta \underline{S}_{mix} = -k\left[X_A \ln X_A + X_B \ln X_B\right]$

(iii) chemical potentials

$X = X_B$

$\Delta \underline{G}_{mix}$

$\mu_B - \mu_B^{\circ}$

$\mu_A - \mu_A^{\circ}$
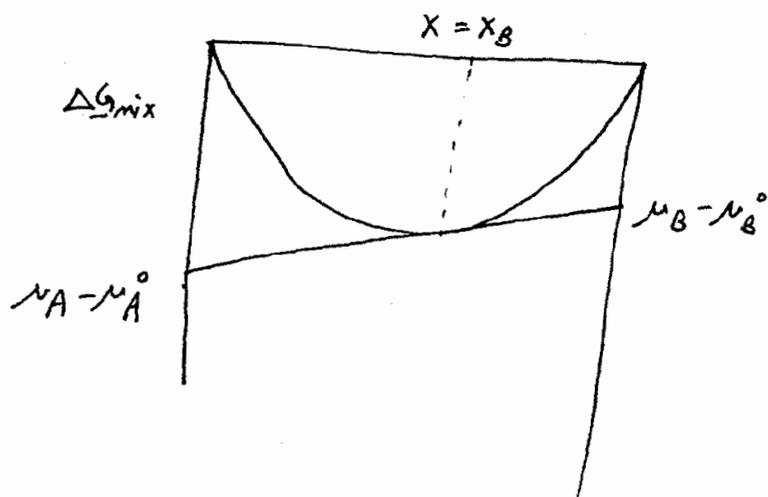
$$\begin{cases} \mu_A - \mu_A^{\circ} = \Delta \underline{G}_{mix}(x) - \frac{d\Delta \underline{G}_{mix}}{dx} x = Z\omega x^2 + RT \ln(1-x) \\[4mm] \mu_B - \mu_B^{\circ} = \Delta \underline{G}_{mix}(x) + \frac{d\Delta \underline{G}_{mix}}{dx}(1-x) = \ \ \rule{2cm}{0.4pt} \\[3mm] \hspace{6cm} Z\omega(1-x)^2 + RT \ln x \end{cases}$$

PROBLEM 4 (LEVEL 2)

a)(iv) Activities

For B,
$$RT \ln a_B = z\omega(1-x)^2 + RT \ln x$$

$$\ln a_B = \frac{z\omega}{RT}(1-x)^2 + \ln x$$

$$\boxed{a_B = x \exp\left(\frac{z\omega}{RT}(1-x)^2\right)}$$

b) $\Delta \underline{G}_{mix}$ at different temperatures

T = 200 k

T = 250 k

T = 300 k

T = 350 k

Gibbs free energy (J/mol)

x = concentration of B specie

CHEMICAL POTENTIAL $\mu_B - \mu_B^o$

x = concentration of specie B

chemical potential (J/mol)

200 k

300 k

200 k

x = concentration of B

chemical potential (J/mol)

$\mu_B - \mu_B^o$

$\mu_A - \mu_A^o$
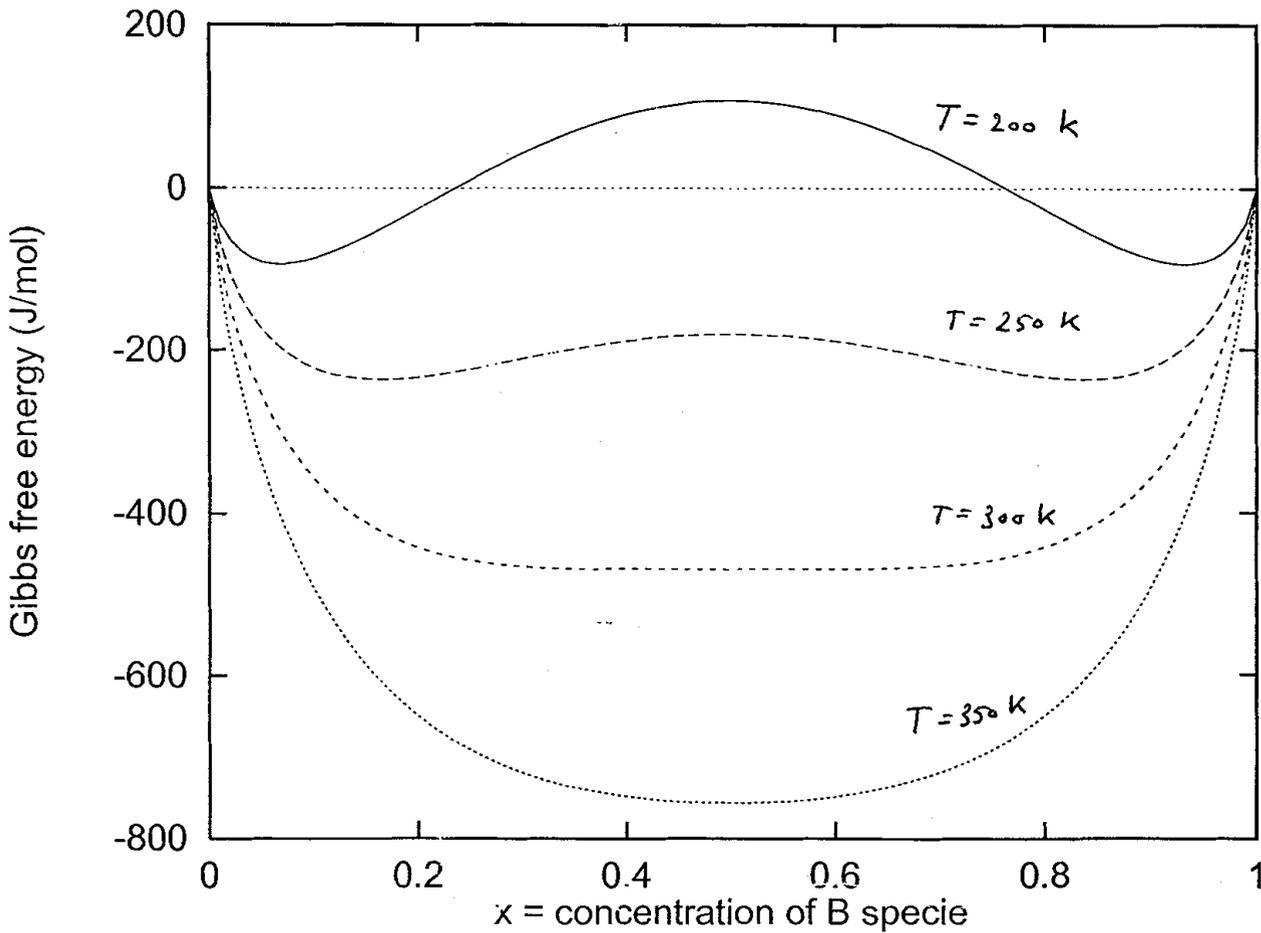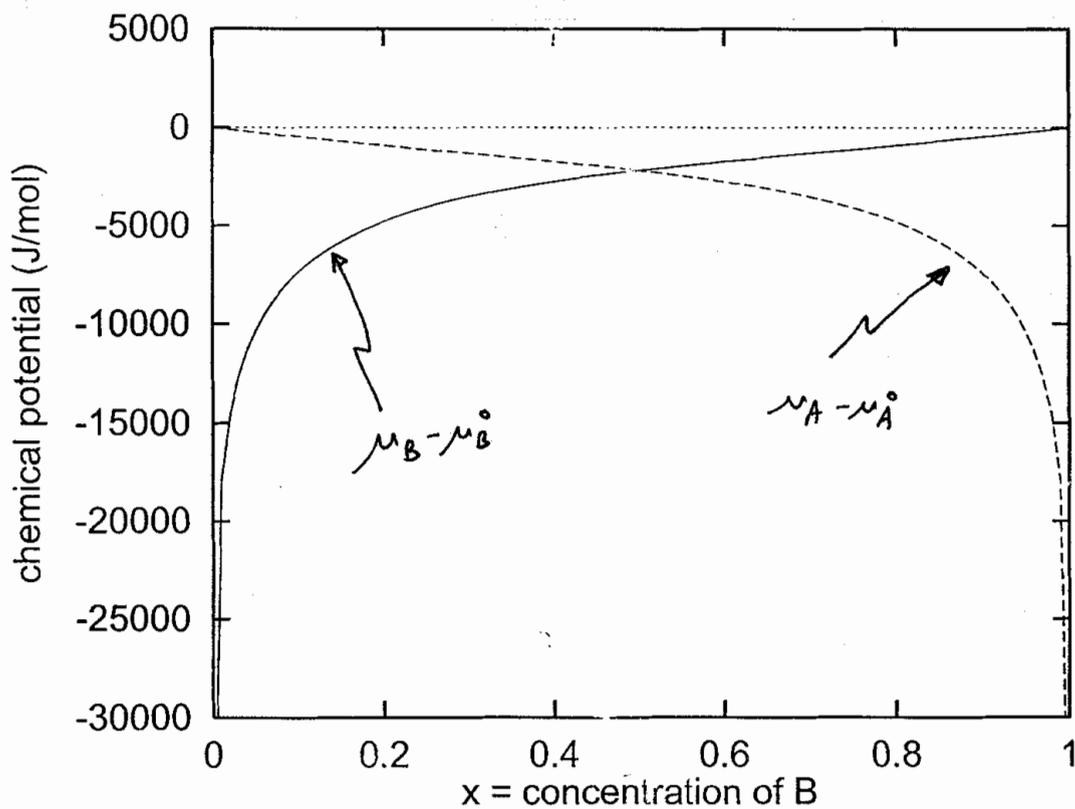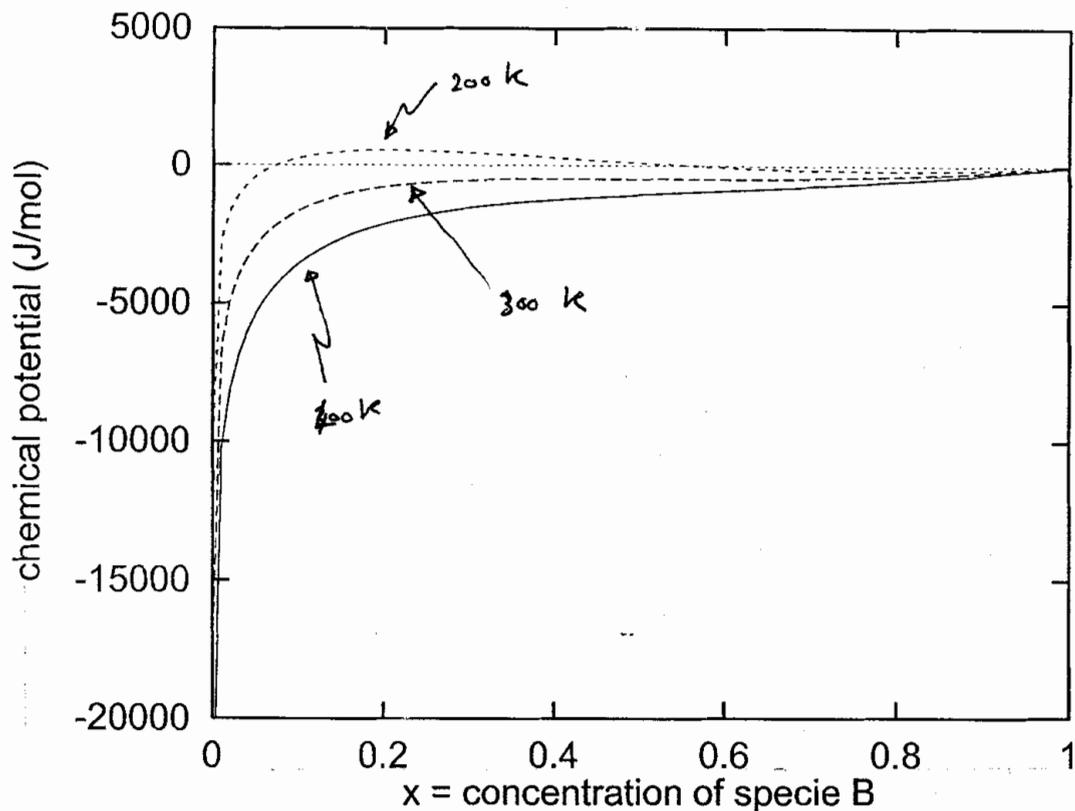
Activity of B

PROBLEM 5 (LEVEL 2)

$$CO_2 \quad + \quad H_2 \quad = \quad CO \quad + \quad H_2O$$
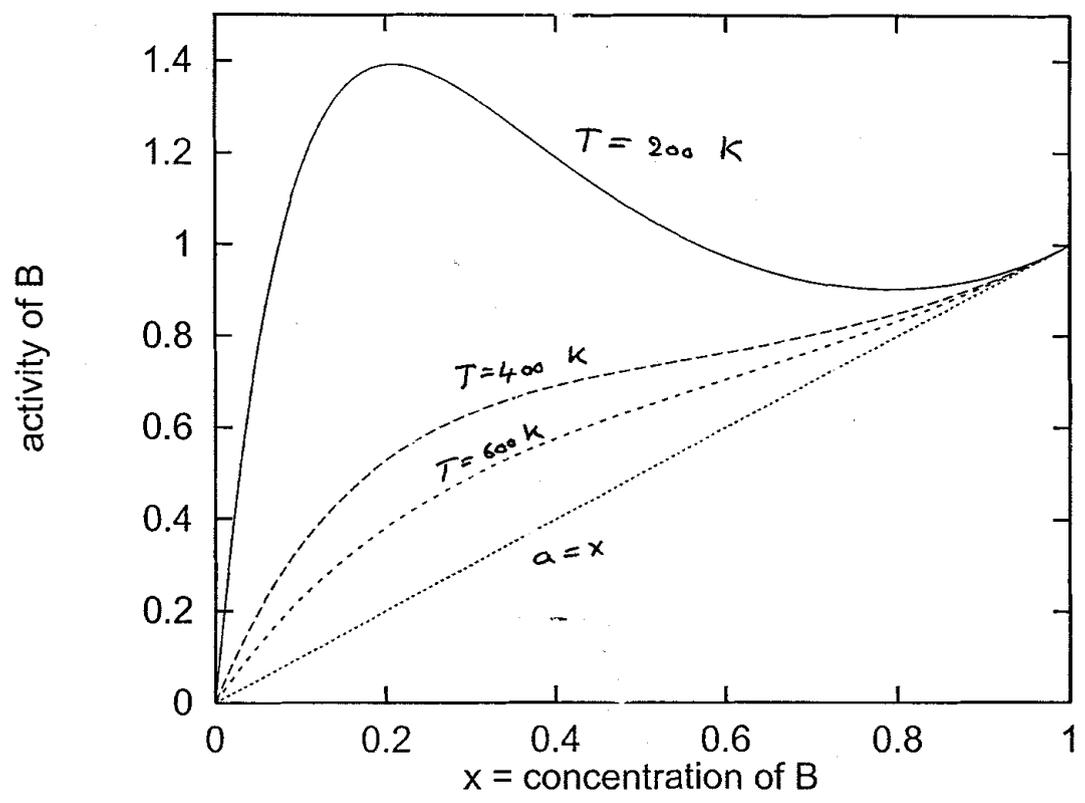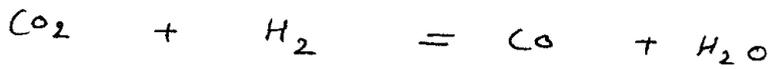
initial
state $\quad\quad$ 0.2 $\quad\quad\quad$ 0.5 $\quad\quad\quad$ 0.2 $\quad\quad\quad$ 0.1

final
state $\quad\quad$ 0.2-λ $\quad\quad$ 0.5-λ $\quad\quad$ 0.2+λ $\quad\quad$ 0.1+λ

where λ = progress variable of the reaction

* Equilibrium constant of the reaction :

$$K = \frac{P_{CO} \, P_{H_2O}}{P_{CO_2} \, P_{H_2}} \qquad \text{with} \quad P_i = \left(\frac{n_i}{n_{total}}\right) P$$

$$\Rightarrow \boxed{K = \frac{(0.2+\lambda)(0.1+\lambda)}{(0.2-\lambda)(0.5-\lambda)}} \qquad (1)$$

* we also know that

$$K = \exp\left(\frac{-\Delta G°}{RT}\right) \qquad \text{with} \quad \Delta G° = \mu°_{CO_2} + \mu°_{H_2} - \mu°_{CO} - \mu°_{H_2O}$$

as is given, $\Delta G° = -2300$ cal $\quad$ at 1500 K

$$\Rightarrow \boxed{K = 2.16} \qquad (2)$$

solving (1) and (2) yields

$$\boxed{\lambda_{eq} = 0.117} \quad\Longrightarrow$$

in the final state
we have:

8.3 % $\quad CO_2$

38.3 % $\quad H_2$ $\quad$ and $\quad$ 21.7 % $\quad H_2O$

31.7 % $\quad CO$

PROBLEM 6   (LEVEL 2)

* Fe acts as a host for C atoms which occupy interstitial sites in the bcc structure of Fe.

* Assume we have 1 mole of Fe in the bcc structure (i.e. N_A Fe atoms). Then we have $3N_A$ interstitial sites available for C.

* Assume we take n C atoms from its pure reference state (e.g. graphite) and insert them into the Fe crystal. (we consider dilute C concentration such that $n < N_A$)

Then:

$$\Delta H = \frac{n}{N_A} E_i$$

$$\Delta S = k \ln \left| \frac{(3N_A)!}{(3N_A - n)! \, n!} \right| = k \left[\ln(3N_A)! - \ln(3N_A - n)! - \ln n! \right]$$

Stirling
$$= k \left[3N_A \ln \left(\frac{3N_A}{3N_A - n} \right) + n \ln \left(\frac{3N_A - n}{n} \right) \right]$$

$$\Delta G = \Delta H - T\Delta S$$

$$= \frac{n}{N_A} E_i + kT \left[3N_A \ln \left(\frac{3N_A - n}{3N_A} \right) + n \ln \left(\frac{n}{3N_A - n} \right) \right]$$

let $y = \frac{n}{N_A}$

PROBLEM 6 (LEVEL 2) CONTINUED

$$\Delta G = y\, E_i + RT\left[3\ln\left(1 - \frac{y}{3}\right) + y\ln\left(\frac{\frac{y}{3}}{1 - \frac{y}{3}}\right)\right]$$

$$= y\, E_i + RT\left[3\ln\left(1 - \frac{y}{3}\right) + y\ln\left(\frac{y}{3}\right) - y\ln\left(1 - \frac{y}{3}\right)\right]$$

$$\boxed{\Delta G = y\, E_i + RT\left[3\left(1 - \frac{y}{3}\right)\ln\left(1 - \frac{y}{3}\right) + y\,\frac{1}{3}\ln\left(\frac{y}{3}\right)\right]}$$

↳ The free energy for $Fe\, C_y$

b) $\mu_C = \dfrac{\partial \Delta G}{\partial\left(\frac{n}{N_A}\right)}$ where $\dfrac{n}{N_A}$ is the number of moles of

C in one mole of Fe

$$\boxed{\mu_C = E_i + RT\,\ln\left(\frac{\frac{y}{3}}{1 - \frac{y}{3}}\right)}$$