Lecture 19

Thermodynamics of Solutions

Dilute solutions and Multi-component Systems

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Today's Topics

- Characteristics of Dilute Solutions and Henry's Law
- Standard States for Dilute Solutions
- Characteristics of Multi-component systems
- Example

Dilute Solutions

What happens when a few atoms of solute A is added in a solvent B ?

Behaviour of solvent atoms

- only a few solvent atoms has solute atoms as neighbour
- the solvent atoms act as if they were in an ideal solution

$$\lim_{X_B \to 1} a_B = X_B$$

Behaviour of solute atoms

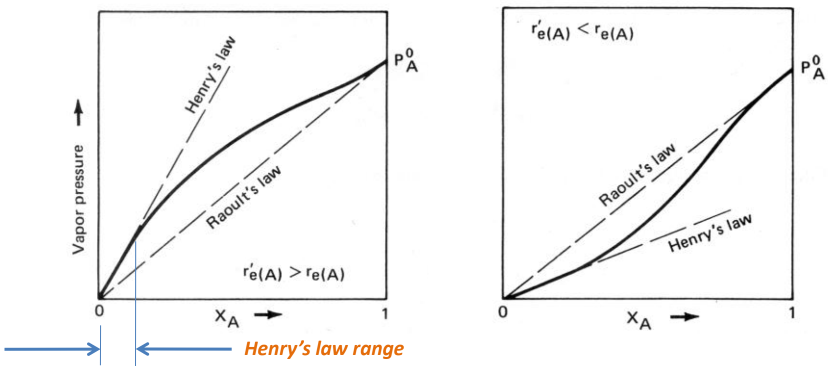
- every solute atom is completely surrounded by solvent atoms
- until a sufficient number of solute atoms are added, each solute atom added to the solution makes the same contribution to the properties of the system
- In this limiting case, the average properties of the solute atoms can be considered as proportional to their concentrations. For example,

$$\lim_{X_A \to 0} p_A \propto X_A$$

- This constitutes **Henry's law** for the solute in a dilute solution:

$$p_A \propto X_A$$

- The proportionality constant of Henry's law:
  - not depends solely upon the solute, but also upon the other components



- The range of composition over which the solute obeys Henry's law:
  - depends on the interaction between the component species
  - the greater the deviation of activity coefficient γ from unity, the more restricted is Henry's law range

- When a solution obeys Henry's law, the activity of solute is expressed as:

$$a_k = \gamma^0_k \cdot X_k$$

Here,

γ^0_k = **Raoultian activity coefficient** of k **at infinite dilution**

= Slope of curve at $X_k=0$

(also known as **Henry's law constant on Raoultian scale**)

- Different forms of Raoults Law:

For ideal solution: $a_k = X_k$

For non-ideal solution: $a_k = \gamma_k \cdot X_k$

For non-ideal dilute solution: $a_k = \gamma^0_k \cdot X_k$

Standard state:
Pure substance
i.e., $a_k=1$ when $X_k=1$

Standard States for Dilute solutions

- a_k=1 for X_k=1 cannot be considered, since for dilute solutions X_k << 1.

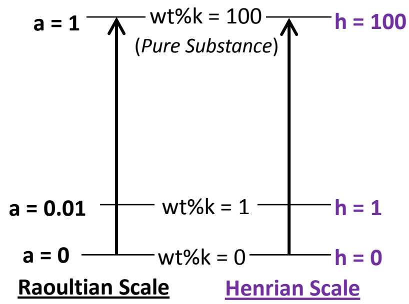
- **Alternate standard states for dilute solutions:**

  1 atom % solution
  i.e., activity = 1 when X_k=0.01.

- In this new scale, Henrian activity

$$h_k = f_k \cdot X_k$$

  h_k = Henrian activity of k
  f_k = Henrian activity coefficient of k



- When X_k=0.01, h_k = 1 and f_k = 1.

- Another alternate standard state for dilute solution:
  1 wt% solution.

- Activity on this scale:

$$h_A = f_A \cdot wt\%A$$

- In this scale, for 1 wt.% solution, h_A=1 so that f_A=1

- **At infinite dilution**,
  As wt.%A $\rightarrow$ 0, $f_A \rightarrow 1$, then $h_A = wt.\%A$

Relationship between the two standard states

$$\frac{\gamma_A}{\gamma^0_A} = f_A$$

$$\frac{a_A}{h_A} = \frac{\gamma_A X_A}{f_A X_A} = \gamma^0_A$$

$$\frac{a_A}{h_A} = \frac{\gamma^0_A X_A}{wt\%A} = \frac{\gamma_A X_A}{f_A\, wt\%A}$$

Example 6.5

The activity coefficient of a component A in an infinitely dilute solution is 0.25. When the mole fraction of A is 0.70, its activity referred to the pure substance is 0.35.

From this data calculate the Henrian activity of the component referred to the infinite dilute solution.

What will be the partial molar free energy of A at 1000 K in this standard?

What will be the difference in free energy due to the change of standard from infinitely dilution to pure species?

Answer:

Here the given data: $\gamma^0_A = 0.25$, $X_A=0.70$ and $a_A=0.35$.

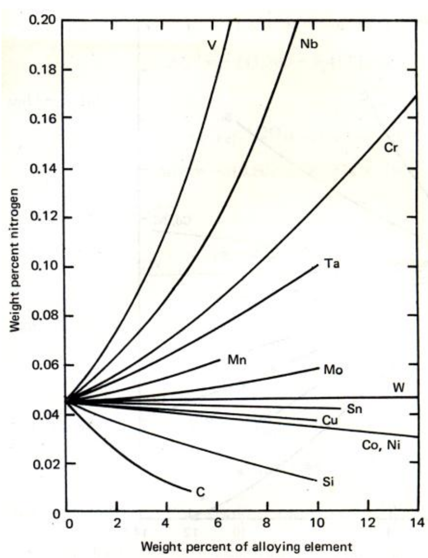
Now the activity coefficient referred to the pure species
$\boldsymbol{\gamma_A = a_A / X_A}$ = 0.35/0.70 = 0.50
And the activity coefficient referred to the infinite dilute solution
$\boldsymbol{f_A = \gamma_A / \gamma^0_A}$ = 0.50 / 0.25 = 2.0

Then the activity of A referred to the infinite dilute solution is
$\boldsymbol{h_A = f_A X_A}$ = 2.0 x 0.70 = 1.40

Now the partial molar free energy of A referred to the infinite dilution is
= RT ln h_A = (8.314 J/mol/K) (1000 K) ln 1.40 = 2797.43 J/mol
Again the partial molar free energy of A referred to the pure species is
= RT ln a_A = (8.314 J/mol/K) (1000 K) ln 0.35 = - 8728.22 J/mol

Thus, the difference in free energy due to the change of standard would be
= 2797.43 – (-8728.22) = 11525.65 J/mol.

Multi-component Systems



Effect of alloy additions on the solubility of nitrogen in binary iron alloys at 1 atm pressure and 1592 °C temperature

- In binary solutions, the behaviour of the solute is determined by the nature and magnitude of the **interactions between the solute and the solvent particles**.
- For multi-component solutions, the **interactions between the solutes** also must be taken into consideration.
- For example, when a second dilute solute C is added to A-B dilute solution, three types of interactions would occur, namely, A-B, C-B and B-C, and the thermodynamic behaviour of the system will be determined by the relative magnitudes of these three types of interaction.

Example: Dilute solution of carbon in iron

- For Fe-C dilute solution, the Henrian activity coefficient of C is f_C.
- If another dilute solute Si is added, then Henrian activity coefficient of C becomes

$$f_C = f_C^C \cdot f_C^{Si} \qquad (6.57)$$

where f_C^{Si} is called the **interaction coefficient** and it measures the effect of silicon on the activity coefficient of carbon.

- Thus, using Eq.(6.57), the Henrian activity of carbon in liquid iron containing C and Si can be calculated by

$$h_C = f_C^C \cdot f_C^{Si} \cdot \text{wt\% C} \qquad (6.58)$$

- When several solutes present (for example, C, Si, Mn, S, and P), the activity coefficient of carbon in this multi-component solution will be

$$f_C = f_C^C \cdot f_C^{Si} \cdot f_C^{Mn} \cdot f_C^S \cdot f_C^P \qquad (6.59)$$

- The equation, however, is only **an approximate one** because it does not take into consideration of any interaction between the solutes silicon, manganese, sulphur and phosphorous.

- For low concentration of k in solution, the interaction coefficient of k on C can be taken as

$$\log f_C^k = e_C^k \cdot \text{wt\% k} \qquad (6.60)$$

Here e_C^k is called the **interaction parameter on Henrian scale**, and it expresses the effect of k on C in the ternary Fe-C-k solution.

$$f_C = f_C^C \cdot f_C^{Si} \cdot f_C^{Mn} \cdot f_C^S \cdot f_C^P$$

$$\log f_C^k = e_C^k \cdot \text{wt\% } k \qquad h_C = f_C \cdot \text{wt\% C}$$

- Substituting Eq.(6.60) in Eq.(6.59) after taking log, we get the activity coefficient of C in Fe-C-Si-Mn-S-P solution as

$$\log f_C = \log f_C^C + e_C^{Si} \cdot \text{wt\% Si} + e_C^{Mn} \cdot \text{wt\% Mn} + e_C^S \cdot \text{wt\% S} + e_C^P \cdot \text{wt\% P} \qquad (6.63)$$

- Then the activity of C in Fe-C-Si-Mn-S-P solution will be

$$\log h_C = \log f_C^C + e_C^{Si} \cdot \text{wt\% Si} + e_C^{Mn} \cdot \text{wt\% Mn} + e_C^S \cdot \text{wt\% S} + e_C^P \cdot \text{wt\% P} + \log \text{wt\% C} \qquad (6.64)$$

- If C interacts more strongly with k than with the iron, then e_C^k will be negative because the addition of k lowers the activity of C in the liquid iron. If, on the other hand, C interacts more strongly with the iron than k, e_C^k will be positive, and hence h_C will increase as k is added.

- The similar treatment can be done in terms of **Raoultian activity** when the pure species is used as the standard state.

- Thus, for Fe-C-Si-Mn-S-P solution, the Raoultian activity and activity coefficient of carbon be

$$a_C = \gamma_C \cdot X_C$$

$$\gamma_C = \gamma_C^C \cdot \gamma_C^{Si} \cdot \gamma_C^{Mn} \cdot \gamma_C^S \cdot \gamma_C^P$$

- Here the interaction coefficient g_C^k can be taken as

$$\ln \gamma_C^k = \varepsilon_C^k \cdot X_k \qquad (6.61)$$

Here ε_C^k is called the **interaction parameter on Raoultian scale**, and it expresses the effect of k on C in the ternary Fe-C-k solution.

- So the Raoultian activity coefficient of C in Fe-C-Si-Mn-S-P solution will be

$$\ln \gamma_C = \ln \gamma_C^C + \varepsilon_C^{Si} . X_{Si} + \varepsilon_C^{Mn} . X_{Mn} + \varepsilon_C^{S} . X_S + \varepsilon_C^{P} . X_P$$

- and the Raoultian activity of C in Fe-C-Si-Mn-S-P solution will be

$$\ln a_C = \ln \gamma_C^C + \varepsilon_C^{Si} . X_{Si} + \varepsilon_C^{Mn} . X_{Mn} + \varepsilon_C^{S} . X_S + \varepsilon_C^{P} . X_P + \ln X_C$$

- The relationship between interaction parameters for solutions in liquid iron for Raoultian and Henrian scales is as follows:

$$e_C^k = \frac{0.2425}{M_k} \varepsilon_C^k \qquad \textbf{(6.62)}$$

where M_k is the atomic weight of component k

- If, instead of e_X^Y, the co-efficient e_Y^X is known, then the following **Wagner approximation** can be used for very dilute solutions where the atomic weights of the solutes do not differ very much from that of the solvent.

$$e_X^Y = \frac{M_X}{M_Y} e_Y^X \qquad \textbf{(6.65)}$$

Example 6.6

The activity coefficient of Zn relative to the infinitely dilute standard state in a binary Bi-Zn solution containing 0.015 wt% Zn at 450 °C is 3.974. Calculate the activity coefficient of Zn in a Bi-Zn-Pb-Au solution containing wt% of Zn, Pb and Au equal to 0.015 at 450 °C. The interaction parameters in bismuth are: $e_{Zn}^{Pb} = 1.3$, $e_{Zn}^{Au} = -2.5$.

Answer:

From Eq.(6.57), it follows that,

$\log f_{Zn} = \log f_{Zn}^{Zn} + \log f_{Zn}^{Pb} + \log f_{Zn}^{Au}$

$\log f_{Zn} = \log f_{Zn}^{Zn} + e_{Zn}^{Pb}\ \text{wt.\%Pb} + e_{Zn}^{Au}\ \text{wt.\%Au}$

$\log f_{Zn} = \log 3.974 + (1.3)(0.015) + (-2.5)(0.015)$

$f_{Zn} = 3.81$

Next Class

Lecture 20

Thermodynamics of Solutions

The Mixing Process