

Thermodynamics of materials

27. Chemical Potentials of Solutions IV

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Chemical Potentials of Ideal Solution

- For ideal solution,

$$\mu_i = \mu_i^\circ + RT \ln x_i$$

the chemical energy potential change for one more of species i from the pure state to solution is

$$\Delta\mu_i = RT \ln x_i$$

and

$$\Delta\mu = RT \sum_{i=1}^n (x_i \ln x_i)$$

- Since it is the ideal solution,

$$\Delta h = 0$$



Chemical Potentials of Ideal Solution

- The entropy change for one mole of component i from the pure state to solution is

$$\Delta s_i = - \left(\frac{\partial \Delta \mu_i}{\partial T} \right)_{p, x_i} = -R \ln x_i$$

and the entropy of mixing is

$$\Delta s = - \left(\frac{\partial \Delta \mu}{\partial T} \right)_{p, x_i} = -R \sum_{i=1}^n (x_i \ln x_i)$$

the volume of mixing for an ideal solution is zero

$$\Delta v = \left(\frac{\partial \Delta \mu}{\partial p} \right)_{T, x_i} = 0$$



Chemical Potentials of Ideal Solution

- We have the relations for a binary solution:

$$\mu = (x_A \mu_A^\circ + x_B \mu_B^\circ) + RT(x_A \ln x_A + x_B \ln x_B)$$

$$\Delta\mu = \mu - (x_A \mu_A^\circ + x_B \mu_B^\circ) = RT(x_A \ln x_A + x_B \ln x_B)$$

$$\Delta\mu_A = \mu_A - \mu_A^\circ = RT \ln x_A$$

$$\Delta\mu_B = \mu_B - \mu_B^\circ = RT \ln x_B$$

$$\Delta s = -\left(\frac{\partial \Delta\mu}{\partial T}\right)_{p, x_B} = -R(x_A \ln x_A + x_B \ln x_B)$$

$$\Delta s_A = -\left(\frac{\partial \Delta\mu_A}{\partial T}\right)_{p, x_B} = -R \ln x_A$$

$$\Delta s_B = -\left(\frac{\partial \Delta\mu_B}{\partial T}\right)_{p, x_A} = -R \ln x_B$$



- For volume and enthalpy change

$$\Delta v_A = - \left(\frac{\partial \Delta \mu_A}{\partial p} \right)_{T, x_B} = 0$$

$$\Delta v_B = - \left(\frac{\partial \Delta \mu_B}{\partial p} \right)_{T, x_A} = 0$$

$$\Delta h = 0$$

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Chemical Potentials of Regular Solutions

- For regular solution,

$$a_i \neq x_i \quad \Delta h \neq 0 \quad \Delta s = -R \sum_{i=1}^n x_i \ln x_i$$

- For a binary regular solution,

$$RT \ln \gamma_A = \alpha' x_B^2 \quad RT \ln \gamma_B = \alpha' x_A^2$$

which leads to

$$\mu_A - \mu_A^\circ = RT \ln x_A + RT \ln \gamma_A = RT \ln x_A + \alpha' x_B^2$$

$$\mu_B - \mu_B^\circ = RT \ln x_B + RT \ln \gamma_B = RT \ln x_B + \alpha' x_A^2$$



Chemical Potentials of Regular Solutions

- The chemical potential change of forming a binary solution from pure components is

$$\begin{aligned}\Delta\mu &= RT(x_A \ln a_A + x_B \ln a_B) \\ &= RT(x_A \ln \gamma_A + x_B \ln \gamma_B) + RT(x_A \ln x_A + x_B \ln x_B) \\ &= \alpha'(x_A x_B^2 + x_A^2 x_B) + RT(x_A \ln x_A + x_B \ln x_B) \\ &= \alpha' x_A x_B + RT(x_A \ln x_A + x_B \ln x_B) \\ &= \Delta h - T\Delta s\end{aligned}$$

therefore, we have

$$\Delta h = \alpha' x_A x_B$$

and

$$\Delta s = -R(x_A \ln x_A + x_B \ln x_B)$$



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Chemomechanical Potentials of Components in a Solution

- When the lattice parameter follows Vegard's law,

$$a(c) = a(c_0) + \frac{da}{dc}(c - c_0)$$

where $a(c_0)$ is the lattice parameter of the solution with the reference solute concentration c_0 , and da/dc is the rate of change in lattice parameter with respect to concentration.

- The lattice expansion parameter is

$$\varepsilon_0 = \frac{1}{a(c_0)} \frac{da}{dc} = \frac{a(c) - a(c_0)}{a(c_0)(c - c_0)} = \frac{v_m}{a(c_0)} \frac{da}{dx}$$

where x is the mole fraction of solute atoms, and $v_m = x/c$ is molar volume of the solution.



Chemomechanical Potentials of Components in a Solution

- The concentration-dependent eigenstrain tensor ε_{ij}° can be expressed as

$$\varepsilon_{ij}^{\circ} = \varepsilon_0(c - c_0)\delta_{ij}$$

where δ_{ij} is the Kronecker delta function.

- The elastic strain $\varepsilon_{ij}^{\text{el}}$ is given by

$$\varepsilon_{ij}^{\text{el}} = \varepsilon_{ij} - \varepsilon_{ij}^{\circ} = \varepsilon_{ij} - \frac{1}{a_0}(c - c_0)\delta_{ij} = \varepsilon_{ij} - \varepsilon_0(c - c_0)\delta_{ij}$$

where ε_{ij} is the total strain containing both the elastic strain and compositional strain.

- The total elastic strain, $\varepsilon_{ij}^{\text{el}}$, of an inhomogeneous solid solution is obtained by solving the mechanical equilibrium equation.
- We will assume that the local elastic displacements, elastic strains, and thus the elastic stresses are all available.



Chemomechanical Potentials of Components in a Solution

- The corresponding elastic stresses σ_{ij}^{el} is given by

$$\sigma_{ij}^{\text{el}} = C_{ijkl} \varepsilon_{ij}^{\text{el}}$$

where C_{ijkl} is the elastic modulus tensor.

- The chemomechanical potential μ^{cm} of solute atoms is given by

$$\mu^{\text{cm}} = \sigma_{ij}^{\text{el}} \frac{d\varepsilon_{ij}^{\text{el}}}{dc} + \mu = -\sigma_{ij}^{\text{el}} \varepsilon_0 \delta_{ij} + \mu$$

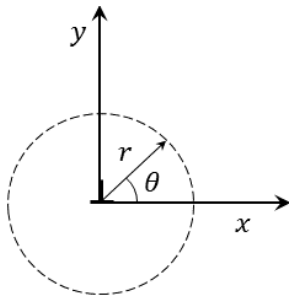
where σ_{ij}^{el} is the local elastic stress, and μ is chemical potential of solute atoms.

- The term, $-\sigma_{ij}^{\text{el}} \varepsilon_0 \delta_{ij}$, is therefore the mechanical contribution to the total chemomechanical potential, μ^{cm} .



Chemomechanical Potentials of Components in a Solution

- Consider a relatively simple example on the segregation of solute B atoms around an edge dislocation for which the elastic solution is available. Assume the edge dislocation is located at $(x = 0, y = 0)$.



Chemomechanical Potentials of Components in a Solution

- The stress distribution around such an edge dislocation with a Burgers vector magnitude of B is given by

$$\sigma_{xx}^{\text{el}} = -\frac{Gb}{2\pi(1-\nu)} \frac{y(3x^2 + y^2)}{(x^2 + y^2)^2}$$

$$\sigma_{yy}^{\text{el}} = -\frac{Gb}{2\pi(1-\nu)} \frac{y(x^2 - y^2)}{(x^2 + y^2)^2}$$

$$\sigma_{zz}^{\text{el}} = -\frac{Gb}{2\pi(1-\nu)} \frac{y}{(x^2 + y^2)}$$

where G is the shear modulus, and ν is the Poisson ratio.



Chemomechanical Potentials of Components in a Solution

- Therefore, the mechanical contribution to the chemomechanical potential of solute atoms around an edge dislocation is

$$-\varepsilon_0 \sigma_{ij}^{\text{el}} \delta_{ij} = -\varepsilon_0 (\sigma_{xx}^{\text{el}} + \sigma_{yy}^{\text{el}} + \sigma_{zz}^{\text{el}}) = \frac{\varepsilon_0 G b}{\pi} \frac{y}{(x^2 + y^2)} = \frac{\varepsilon_0 G b \sin \theta}{\pi r}$$

where r is the distance from the origin, and θ is the angle from the positive x -axis.



Chemomechanical Potentials of Components in a Solution

- Assume that the mole fraction of solute B atoms in the solution in the absence of dislocations or very far away from the dislocation is x_B° and that the behavior of B atoms can be approximated using ideal solution model.

$$\mu_B^b = \mu_B^\circ + RT \ln x_B^\circ$$

where μ_B^b is the bulk chemical potential without the mechanical contribution, and μ_B° is the chemical potential of B at standard state, i.e., the chemical potential of pure solid B.

- In the presence of an edge dislocation,

$$\mu_B^{\sigma,d} = \mu_B^\circ + RT \ln x_B + \frac{\varepsilon_0 G b \sin \theta}{\pi r}$$



Chemomechanical Potentials of Components in a Solution

- At equilibrium,

$$\mu_{\text{B}}^{\sigma, \text{d}} = \mu_{\text{B}}^{\text{b}}$$

or

$$\mu_{\text{B}}^{\circ} + RT \ln x_{\text{B}} + \frac{\varepsilon_0 G b \sin \theta}{\pi r} = \mu_{\text{B}}^{\circ} + RT \ln x_{\text{B}}^{\circ}$$

proceed to

$$RT \ln \left(\frac{x_{\text{B}}}{x_{\text{B}}^{\circ}} \right) = - \frac{\varepsilon_0 G b \sin \theta}{\pi r}$$

therefore,

$$\frac{x_{\text{B}}}{x_{\text{B}}^{\circ}} = \exp \left(- \frac{\varepsilon_0 G b \sin \theta}{RT \pi r} \right)$$

where x_{B} is the composition distribution of solute atoms around an edge dislocation.



Chemomechanical Potentials of Components in a Solution

- If $\varepsilon_0 > 0$, it implies that the size of B atoms is larger than that of A atoms. For a given r , minimum x_B takes place at $\theta = \pi/2$; i.e., solute B atoms are depleted above the dislocation, and maximum x_B takes place at $\theta = -\pi/2$; i.e., solute B atoms are accumulated below the dislocation.