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Supplementary References

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SOLUTION THERMODYNAMICS: THEORY

In this chapter:

- To develop a fundamental property relation for homogenous solutions of variable composition,
- Partial properties and the mathematical definitions,
- Chemical potential,
- Property relations valid for ideal-gas mixtures,
- Concept of fugacity and the ideal solution,
- Excess properties,
- Concept of activity and the activity coefficient, and so on.

Fundamental Property Relation

Equation expresses the basic relation connecting the Gibbs energy to the temperature and pressure in any **closed system**:

$$d(nG) = (nV)dP - (nS)dT$$

n : the numbers of moles of all chemical species

This closed system is then of constant composition, and we can write immediately that.

$$\left[\frac{\partial(nG)}{\partial P} \right]_{T,n} = nV \quad \text{and} \quad \left[\frac{\partial(nG)}{\partial T} \right]_{P,n} = nS \quad (\text{no chemical reaction})$$

n : the numbers of moles of all chemical species

The derivative of nG with respect to the number of moles of species i has a special significance, and is given its own symbol and name. Thus, we define the chemical potential of species i in the mixture as

$$\mu_i \equiv \left[\frac{\partial(nG)}{\partial n_i} \right]_{P,T,n_j}$$

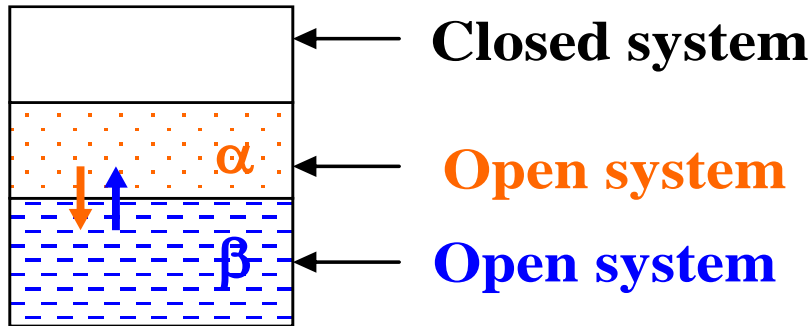
Expressed in terms of μ_i , the general equation for $d(nG)$ is

$$d(nG) = (nV)dP - (nS)dT + \sum_i \mu_i dn_i$$

fundamental property relation for single-phase fluid systems of constant or variable mass and constant or variable composition.

Chemical Potential as a Criterion for Phase Equilibria

Consider a **closed system** consisting of **two phases in equilibrium**. Within this closed system, each of the individual phases is an **open system**, free to transfer mass to the other.



Equation 10.2 may therefore be written for each phase:

$$d(nG)^\alpha = (nV)^\alpha dP - (nS)^\alpha dT + \sum_i \mu_i^\alpha dn_i^\alpha$$

Partial Properties

The definition of the chemical potential by Eq.

$$\left(\mu_i \equiv \left[\frac{\partial(nG)}{\partial n_i} \right]_{P,T,n_j} \right)$$
 as the mole-number derivative of nG

suggests that such derivatives may be of particular use in solution thermodynamics. Thus we write

$$\bar{M}_i \equiv \left[\frac{\partial(nM)}{\partial n_i} \right]_{P,T,n_j}$$

This equation defines the **partial molar property** \bar{M}_i of species **i** in solution, where \bar{M}_i may represent the partial molar internal energy \bar{U}_i and so on....

\bar{M}_i the partial molar internal energy

the partial molar enthalpy

the partial molar entropy

the partial molar Gibbs energy

\bar{U}_i

\bar{H}_i

\bar{S}_i

\bar{G}_i etc.

From partial properties ? calculation of solution properties

$$nM = M(P, T, n_1, n_2, \dots, n_i, \dots)$$

It is possible also to calculate solution properties from partial properties

The total differential of **nM**

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

where subscript **n** indicates that all mole numbers are held constant, and subscript **n_j** that all mole numbers except **n_i** are held constant.

For differentiation at constant composition we may write x instead of n

$$d(nM) = n \left(\frac{\partial M}{\partial P} \right)_{T,x} dP + n \left(\frac{\partial M}{\partial T} \right)_{P,x} dT + \sum_i \bar{M}_i dn_i$$

10.9

where subscript x denotes differentiation at constant composition.

Since $n_i = x_i n$

$$dn_i = x_i dn + n dx_i$$

Replacing dn_i by this expression and replacing $d(nM)$ by the identity

$$d(nM) \equiv ndM + Mdn$$

we write Eq. as

$$ndM + Mdn = n \left(\frac{\partial M}{\partial P} \right)_{T,x} dP + n \left(\frac{\partial M}{\partial T} \right)_{P,x} dT + \sum_i \bar{M}_i (x_i dn + n dx_i)$$