

Title : Introduction to Phase Equilibria

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Source of information : “A Textbook of Chemical Engineering Thermodynamics”

By K. V. Narayan and “Introduction to Chemical Engineering Thermodynamics”

By J. M. Smith, H. C. Van Ness, M. M. Abbott

CRITERIA OF PHASE EQUILIBRIUM

- Consider a homogeneous system in a state of thermodynamic equilibrium, it involves simultaneous thermal and mechanical equilibrium within a system.
- Apart from these constraints, the system must also be in a state of chemical equilibrium.
- A system can interact with the surroundings reversibly or irreversibly.
- In the reversible process, a state of equilibrium is maintained throughout the process. So it can be treated as a process connecting a series of equilibrium states.
- The process can be reversed by an infinitesimal change in the potential for the system or the surroundings.
- The irreversible process, in contrast, occurs with a finite driving force, and it can not be reversed by infinitesimal changes in the external conditions.
- However, all irreversible processes tend towards a state of equilibrium.

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- As per Clausius inequality $ds \geq \frac{dQ}{T}$
 - The equality sign refers to a reversible process which can be treated as a succession of equilibrium states and the inequality refers to the entropy change for a spontaneous process whose ultimate result would be an equilibrium state.
 - As per 1st law of Thermodynamics $dQ = dU + dW$
 - From the above two equation, we get $Tds \geq dU + dW$
 - So, $dU \leq Tds - PdV \dots \dots \dots (1)$
 - Eq. 1 can be treated as the combined statement of the first and second law of thermodynamics applied to a closed system which interact with its surroundings.
 - This equation is utilised for deriving the criteria of equilibrium under various sets of constraints, each set corresponding to a physically realistic or commonly encountered situation.

Constant U and V

- If U & V Constant then Eq. 1 changes to

$$dS_{U,V} \geq 0$$

- The entropy is constant in a reversible process and increases in a spontaneous process occurring in a system of constant U and V.
- Since an irreversible process leads the system to an equilibrium state, the entropy is maximum at equilibrium when no further spontaneous processes are possible.

Constant T and V

➤ Helmholtz free energy is defined as $A = U - TS$

➤ Rearranging and differentiating above Eq., we get

$$dU = dA + TdS + SdT$$

➤ Substituting value in Eq. 1, we get

$$dA \leq -PdV - SdT$$

➤ At T & V Constant then

$$dA_{T,V} \leq 0$$

➤ The spontaneous process occurring at constant temperature and volume, in a state of thermodynamic equilibrium under these conditions the Helmholtz free energy or the work function is a minimum.

Constant P and T

➤ Gibbs free energy define as $G = H - TS = U + PV - TS$

➤ Differentiating above Eq., We get

$$dG = dU + PdV + VdP - TdS - SdT$$

➤ By combining above eq. with eq. 1 we get,

$$dG \leq VdP - SdT$$

➤ At Constant P & T

$$dG_{P,T} \leq 0$$

➤ The free energy either decreases or remains unaltered depending upon whether the process is spontaneous or reversible.

➤ **It implies that The equilibrium state of a closed system is that state for which the total Gibbs energy is a minimum with respect to all possible changes at the given T and P.**

Derivation of the Phase Rule

- Consider a non-reactive system under equilibrium, with π phases each containing N independent chemical species. The degrees of freedom for the system, i.e., the number of intensive variables that may vary independently of each other would be given by:

Degrees of freedom = Total number of systemic intensive variables – number of independent equations relating all the variables.

- Total number of systemic intensive variables (also called the phase rule variables) = T , P and $(N-1)$ species mole fractions for each of the π phases
- Number of independent relations connecting the phase rule variables = $N(\pi-1)$
- Thus the phase rule may be rewritten as:
$$F = [2 + (N - 1)\pi] - [N(\pi - 1)] = 2 + N - \pi$$
- The actual mass of each of the species present are not considered as phase rule variables, as they cannot influence the intensive state of the system.
- A special case of the phase rule obtains for closed systems for which the initial mass for each species is fixed.

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- Since no mass can enter or leave the system, the extensive state of the system is rendered fixed along with the intensive variables.
 - Therefore, apart from the $N(\pi-1)$ constraining relations involving the species chemical potentials, there is an additional $(N-1)\pi$ constraint on the mass of each species.
 - This follows from the fact that if a quantum of a species leaves a phase it must reappear in another or more. Thus the phase rule eqn. leads to

$$F = [2 + (N - 1)\pi] - [(\pi - 1)N] - [(N - 1)\pi] = 2$$

- **The above equation is known as the Duhem's theorem.**
- It implies that for any closed system formed initially from given masses of a number of chemical species, the equilibrium state is completely determined when any two independent variables are fixed.
- The two independent variables that one may choose to specify may be either intensive or extensive. However, the number of independent intensive variables is given by the phase rule.
- Therefore, it follows that when $F = 1$, at least one of the two variables must be extensive, and when $F = 0$, both must be extensive.