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GIBB'S PHASE RULE

The phase rule was developed by Willard Gibbs. It may be used to determine the number of thermodynamic variables within a system at equilibrium. The thermodynamic variables are normally T, P, and composition. Although the phase rule may be modified to account for pressure differences caused by osmosis or surface tension, the following equations apply only to systems in which the pressure is uniform. The number of variables which must be fixed must equal the number of degrees of Freedom F. The value of F may be calculated as

$$F = C - P + 2$$

Where

$$C = \left\{\begin{array}{c}\text{Total number of} \\ \text{constituents}\end{array}\right\} - \left\{\begin{array}{c}\text{Number of indepen-} \\ \text{dent reactions}\end{array}\right\} - \left\{\begin{array}{c}\text{Number of independent} \\ \text{restricting equations}\end{array}\right\}$$

P = number of homogeneous, physically, distinct, mechanically separable portions of a system.

It must be remembered that the phase rule can only be applied to systems at equilibrium. The following are physical conditions which are fulfilled at true equilibrium conditions.

1. The system is sensitive to changes in external conditions.
2. Concentrations are independent of time.
3. Equilibrium is independent of the masses of a system's phases.
4. The same concentrations are reached regardless of the direction equilibrium is approached.

Of course, the thermodynamic criterion of equilibrium is when $\Delta G = 0$.

Example: $CaCO_{3(S)} = CaO_{(S)} + CO_{2(g)}$

$C = 3 - 1 - 0 = 2$
$P = 3$
$F = 2 - 3 + 2 = 1$

Therefore, if T is specified, P is fixed (i.e., P_{CO_2}). If P is specified, then T is fixed.