# Phase Diagrams and the Relative Stability of Solids, Liquids, and Gases

## 3 The Phase Rule

- *The term* ***phase*** *($P$) signifies a state of matter that is uniform throughout, not only in chemical composition but also in physical state*
- *A solution of sodium chloride in water is a single phase ($P$ = 1)*
- *Ice is a single phase ($P$ = 1)*
- *A slurry of ice and water is a two-phase system ($P$ = 2)*
- *An alloy of two metals is a two-phase system ($P$ = 2) if the metals are immiscible, but a single-phase system ($P$ = 1) if they are miscible*

# 3 The Phase Rule

- *A **constituent** of a system means a chemical species (an ion or a molecule) that is present*
- *A mixture of ethanol and water has two constituents*
- *A solution of sodium chloride has three constituents: water, $Na^+$ ions, and $Cl^-$ ions*
- *A **component** is a chemically independent constituent of a system*
- *The number of components ($C$) in a system is the minimum number of independent species necessary to define the composition of all the phases present in the system*
- *Pure water is a one-component system ($C = 1$)*
- *A mixture of ethanol and water is a two component system ($C = 2$)*

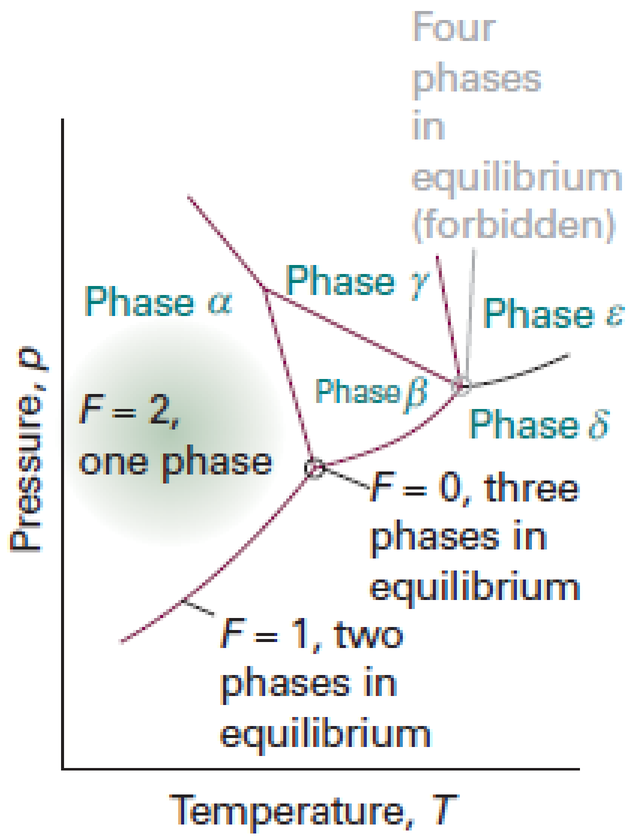
# 3 The Phase Rule

- *An aqueous solution of sodium chloride has* **two components** *because, by charge balance, the number of $Na^+$ ions must be the same as the number of $Cl^-$ ions*

- *The* **variance** *($F$) of a system is the number of intensive variables that can be changed independently without disturbing the number of phases in equilibrium*

- *In a single-component, single-phase system ($C$ = 1, $P$ = 1), the pressure and temperature may be changed independently without changing the number of phases, so $F$ = 2*

- *If two phases are in equilibrium in a single component system ($C$ = 1, $P$ = 2), the variance of the system is fallen to 1*



# 3 The Phase Rule

- *Gibbs deduced the* ***phase rule****, which is a general relation between the variance,* $F$*, the number of components,* $C$*, and the number of phases at equilibrium,* $P$*, for a system of any composition*

$$F = C - P + 2$$

- *Consider first the special case of a one-component system. For two phases in equilibrium,*

$$\mu_\alpha(T, P) = \mu_\beta(T, P)$$



- *This is an equation relating* $P$ *and* $T$*, so only one of these variables is independent (just as the equation* $x + y = 2$ *is a relation for* $y$ *in terms of* $x$*:* $y = 2 - x$

- *That conclusion is consistent with* $F = 1$

# 3 The Phase Rule

- *For three phases in mutual equilibrium,*

$$\mu_{\alpha}(T, P) = \mu_{\beta}(T, P) = \mu_{\gamma}(T, P)$$



- *This relation is actually two equations for two unknowns and therefore has a solution only for a single value of $P$ and $T$ (just as the pair of equations $x + y = 2$ and $3x - y = 4$ has the single solution $x = \frac{3}{2}$ and $y = \frac{1}{2}$). That conclusion is consistent with $F = 0$*

- *Four phases cannot be in mutual equilibrium in a one-component system because the three equalities means there are three equations for two unknowns ($P$ and $T$) and are not consistent (just as $x + y = 2$, $3x - y = 4$, and $x + 4y = 6$ have no solution)*