Molar and Reduced Variables

When dealing with single-component systems, it usually simplifies the algebra to replace all extensive quantities $X_K$ by their molar equivalents $x_k = X_k / N$. Even greater simplifications can be achieved by working with reduced variables, $\bar{x}_k = x_k / x_{k,0}$, $\bar{F}_k = F_k / F_{k,0}$. The features of the extensive, molar, and reduced representations are compared below.

**Extensive** ($X_k$, $F_k$)

- The variables $X_k$ (e.g., $S$, $U$, $V$, $N$) are extensive: $N \to \lambda N \Rightarrow X_k \to \lambda X_k$.
- The conjugate variables $F_k = \partial U / \partial X_k$ are intensive: $N \to \lambda N \Rightarrow F_k \to F_k$.
- In order to be dimensionally correct and to have the correct extensivity/intensivity, each thermodynamic equation may require dimensionful constants and/or factors of $N$, e.g.,
  - extensive: $S = UV / (\theta v_0 N)$ (not $S = UV$);
  - intensive: $T = \theta v_0 N / V$ (not $T = 1 / V$).

**Molar** ($x_k$, $F_k$)

- All variables are intensive: $N \to \lambda N$, $X_k \to \lambda X_k \Rightarrow x_k = X_k / N \to x_k$.
- Any equation should be written solely in terms of $x_k$’s, $F_k$’s, and constants (with no $N$’s).
- If the $x_k$’s in such an equation are replaced everywhere by $X_k / N$, then the resulting equation will have the correct extensivity/intensivity.
- Each equation may still require constants to ensure dimensional correctness, e.g.,
  - molar: $s = uv / \theta v_0$ (not $s = uv$);
  - intensive: $T = \theta v_0 / v$ (not $T = 1 / v$).
- First partial derivatives of the fundamental equation can be taken straightforwardly:
  $F_k = (\partial U / \partial X_k)_N, \ldots = \partial u / \partial x_k = -T \partial s / \partial x_k$.
- Exception: Since $N$ does not appear in the molar representation, $\mu = (\partial U / \partial N)_{S,V}$ must be obtained from $d \mu = -sdT + vdP$ (Gibbs-Duhem) or $\mu = u - Ts + P v$ (Euler).

**Reduced** ($\bar{x}_k$, $\bar{F}_k$)

- All variables are intensive and dimensionless: $\bar{x}_k = x_k / x_{k,0}$, $\bar{F}_k = F_k / F_{k,0}$. Here, $x_{k,0}$ (or $F_{k,0}$) is a reference value which has the same physical dimensions and units as $x_k$ (or $F_k$).
- In a simple, one-component system, all reference values can be expressed using just three basic constants, e.g., $R$ (a molar entropy), $\theta$ (a temperature), and $v_0$ (a molar volume): $\bar{s} = s / R$, $\bar{u} = u / R \theta$, $\bar{v} = v / v_0$, $\bar{T} = T / \theta$, $\bar{P} = P v_0 / R \theta$, and $\bar{\mu} = \mu / R \theta$.
- Any equation should be written solely in terms of $\bar{x}_k$’s, $\bar{F}_k$’s, and dimensionless constants.
- If the reduced variables in such an equation are replaced everywhere by expressions involving $X_k / N$, $F_k$, and reference values, then the resulting equation will have the correct extensivity/intensivity and will be dimensionally correct, e.g.
  - reduced molar: $\bar{s} = \bar{u} \bar{v} \Leftrightarrow S = UV / (\theta v_0 N)$;
  - reduced intensive: $\bar{T} = 1 / \bar{v} \Leftrightarrow T = \theta v_0 N / V$.
- First partial derivatives of the fundamental equation can be taken straightforwardly:
  $\bar{F}_k = \partial \bar{u} / \partial \bar{x}_k = -\bar{T} \partial \bar{s} / \partial \bar{x}_k$.
- Exception: $\bar{\mu}$ must be obtained from $d \bar{\mu} = -\bar{s} d \bar{T} + \bar{v} d \bar{P}$ or $\bar{\mu} = \bar{u} - \bar{T} \bar{s} + \bar{P} \bar{v}$.