1 Equilibrium State and State Variables

The Thermo-Calc software (TCC and TCW) uses Classic Thermodynamics that deals only with systems that are in equilibrium, i.e., in a state stable against internal fluctuations in a number of variables, such as temperature and composition. These variables that have defined values or properties at the equilibrium state are called state variables. Other examples of state variables are pressure (P), and chemical potential ($\mu$). Thermodynamics provides a number of relations between these state variables that make it possible to calculate the value of any other variable at equilibrium.

A state variable can be of two types, extensive or intensive. The value of an extensive variable, e.g., volume, depends on the size of the system, whereas the value of an intensive variable, e.g., temperature, is independent of the size of the system. Each type of state variable has a complementary variable of the other type. The variable complementing the volume is pressure, while the variable complementing the composition of a component is its chemical potential.

It is worth mentioning here that the activity of a component can always be obtained from its chemical potential using a simple mathematical relationship. It is also possible to choose any convenient reference state for the activity or the chemical potential. One of the advantages with a thermodynamic databank on a computer is that, in most cases, such reference state changes can be handled internally without troubling the user.

If the work that can be exchanged with the surroundings is limited to pressure-volume work, the state of equilibrium of a system can be obtained by assigning values to exactly $N+2$ state variables where $N$ is the number of components of the system.

Note that the Thermo-Calc software distinguishes between components of a system and constituent (i.e., species) of a phase in the system. Many state variables require one or the other. By default, the elements are defined as the system components, but this definition can be changed by redefining the components, however, one cannot change the number of components. For instance:

- If the elements are Ca, Si and O, another set of components can be defined as CaO, SiO2 and O2;
- In a pure water system, the components are normally defined as H2O, H+ and ZE (the specially-assigned component for accounting the electro-static state in water); while a number of elements are added into the dissolving H2O system, the component set should be H2O, H+ and ZE, plus the relevant components for the additional elements.

A state variable is a defined thermodynamic quantity under a certain equilibrium state, either for the whole system, or for a component in the system, or a species in a specific substitutional phase, or a constituent (i.e., a species on a specific sublattice site) in a specific phase.

The basic intensive and extensive variables which are suitable in the Thermo-Calc package are listed and briefly described in Table 1, and are also be dealt with in some relevant chapters in the TCCR User’s Guide.
# Thermo-Calc State Variables & Derived Variables

## Table 1. State Variables that can be used in the Thermo-Calc Package

<table>
<thead>
<tr>
<th>Name</th>
<th>Mnemonic</th>
<th>Possible Units</th>
<th>Meaning</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Intensive variables</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T</td>
<td>T</td>
<td>K, °C, °F</td>
<td>Temperature</td>
<td>of the whole system</td>
</tr>
<tr>
<td>P</td>
<td>P</td>
<td>Pa, bar, psi</td>
<td>Pressure</td>
<td>of the whole system</td>
</tr>
<tr>
<td>μ</td>
<td>MU(comp)</td>
<td>J/mol, cal/mol</td>
<td>Chemical potential</td>
<td>of a component in the system</td>
</tr>
<tr>
<td></td>
<td>MU(sp,ph)</td>
<td></td>
<td></td>
<td>of a species in a solution phase</td>
</tr>
<tr>
<td>a</td>
<td>AC(comp)</td>
<td>dimensionless</td>
<td>Activity</td>
<td>of a component in the system</td>
</tr>
<tr>
<td></td>
<td>AC(sp,ph)</td>
<td></td>
<td></td>
<td>of a species in a solution phase</td>
</tr>
<tr>
<td></td>
<td>LNAC(comp)</td>
<td></td>
<td>ln(Activity)</td>
<td>of a component in the system, in natural logarithm ((\ln AC = \frac{\mu}{RT}))</td>
</tr>
<tr>
<td></td>
<td>LNAC(sp,ph)</td>
<td></td>
<td></td>
<td>of a species in a solution phase, in natural logarithm ((\ln AC = \frac{\mu}{RT}))</td>
</tr>
<tr>
<td><strong>Extensive variables – Energetic (for the whole system or for a phase)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>V</td>
<td>m³, dm³, cm³</td>
<td>Volume</td>
<td>of the whole system</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>of a phase</td>
</tr>
<tr>
<td>G</td>
<td>G</td>
<td>J, cal</td>
<td>Gibbs energy</td>
<td>of the whole system</td>
</tr>
<tr>
<td></td>
<td>G(ph)</td>
<td></td>
<td></td>
<td>of a phase</td>
</tr>
<tr>
<td>A</td>
<td>A</td>
<td>J, cal</td>
<td>Helmholtz energy</td>
<td>of the whole system</td>
</tr>
<tr>
<td></td>
<td>A(ph)</td>
<td></td>
<td></td>
<td>of a phase</td>
</tr>
<tr>
<td>U</td>
<td>U</td>
<td>J, cal</td>
<td>Internal energy</td>
<td>of the whole system</td>
</tr>
<tr>
<td></td>
<td>U(ph)</td>
<td></td>
<td></td>
<td>of a phase</td>
</tr>
<tr>
<td>H</td>
<td>H</td>
<td>J, cal</td>
<td>Enthalpy</td>
<td>of the whole system</td>
</tr>
<tr>
<td></td>
<td>H(ph)</td>
<td></td>
<td></td>
<td>of a phase</td>
</tr>
<tr>
<td>S</td>
<td>S</td>
<td>J/K, cal/K</td>
<td>Entropy</td>
<td>of the whole system</td>
</tr>
<tr>
<td></td>
<td>S(ph)</td>
<td></td>
<td></td>
<td>of a phase</td>
</tr>
<tr>
<td>C_p</td>
<td>HM,T</td>
<td>J/mol/K, cal/mol/K</td>
<td>Heat capacity at constant P</td>
<td>of the whole system</td>
</tr>
<tr>
<td></td>
<td>HM(ph),T</td>
<td></td>
<td></td>
<td>of a phase</td>
</tr>
<tr>
<td>C_v</td>
<td>HM,T</td>
<td>J/mol/K, cal/mol/K</td>
<td>Heat capacity at constant V</td>
<td>of the whole system</td>
</tr>
<tr>
<td></td>
<td>HM(ph),T</td>
<td></td>
<td></td>
<td>of a phase</td>
</tr>
<tr>
<td>D</td>
<td>DG(ph)</td>
<td>dimensionless</td>
<td>Driving force (thermodynamic factor)</td>
<td>of a phase (already divided by RT). Note this must be used together with a normalizing suffixes, M, W, V or F (see below).</td>
</tr>
<tr>
<td><strong>Extensive variables – Compositional (overall-components amount/size for the whole system, or amount of a component in the system or in a phase)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n</td>
<td>N</td>
<td>mole</td>
<td>Moles</td>
<td>of all components in the system</td>
</tr>
<tr>
<td></td>
<td>N(comp)</td>
<td></td>
<td></td>
<td>of a component in the system</td>
</tr>
<tr>
<td></td>
<td>N(ph,comp)</td>
<td></td>
<td></td>
<td>of a component in a phase</td>
</tr>
<tr>
<td></td>
<td>NP(ph)</td>
<td></td>
<td></td>
<td>of a phase</td>
</tr>
<tr>
<td>b</td>
<td>B</td>
<td>gram</td>
<td>Mass</td>
<td>of all components in the system</td>
</tr>
<tr>
<td></td>
<td>B(comp)</td>
<td></td>
<td></td>
<td>of a component in the system</td>
</tr>
<tr>
<td></td>
<td>B(ph,comp)</td>
<td></td>
<td></td>
<td>of a component in a phase</td>
</tr>
<tr>
<td></td>
<td>BP(ph)</td>
<td></td>
<td></td>
<td>of a phase</td>
</tr>
<tr>
<td>x</td>
<td>X(comp)</td>
<td>dimensionless</td>
<td>Mole fraction</td>
<td>of a component in the system</td>
</tr>
<tr>
<td></td>
<td>X(ph,comp)</td>
<td></td>
<td></td>
<td>of a component in a phase</td>
</tr>
<tr>
<td>w</td>
<td>W(comp)</td>
<td>dimensionless</td>
<td>Mass (weight) fraction</td>
<td>of a component in the system</td>
</tr>
<tr>
<td></td>
<td>W(ph,comp)</td>
<td></td>
<td></td>
<td>of a component in a phase</td>
</tr>
<tr>
<td>x%</td>
<td>X%(comp)</td>
<td>dimensionless</td>
<td>Mole percent</td>
<td>of a component in the system</td>
</tr>
<tr>
<td>w%</td>
<td>W%(comp)</td>
<td>dimensionless</td>
<td>Mass (weight) percent</td>
<td>of a component in the system</td>
</tr>
<tr>
<td>in</td>
<td>IN(sp)</td>
<td>mole</td>
<td>Input mole number</td>
<td>of a phase species into the system</td>
</tr>
<tr>
<td>im</td>
<td>IM(sp)</td>
<td>gram</td>
<td>Input mass unit</td>
<td>of a phase species into the system</td>
</tr>
</tbody>
</table>
### Thermo-Calc State Variables & Derived Variables

#### Extensive variables – Constitutional Composition (amount of a constituent/species on a sublattice site in a phase)

<table>
<thead>
<tr>
<th>y</th>
<th>( y \text{(ph,cons#sub)} )</th>
<th>dimensionless</th>
<th>Site fraction</th>
<th>of a constituent on a sublattice site (denoted by # and a digit) in a phase</th>
</tr>
</thead>
</table>

#### Special quantities

<table>
<thead>
<tr>
<th>Q</th>
<th>( QF \text{(ph)} )</th>
<th>dimensionless</th>
<th>Phase stability function</th>
<th>of a phase (being negative when the phase composition is inside a spinodal or positive elsewhere)</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>( T_c )</th>
<th>( TC \text{(ph)} )</th>
<th>K</th>
<th>Curie temperature</th>
<th>of a phase</th>
</tr>
</thead>
</table>

| \( M_b \)  | \( BMAGN \text{(ph)} \) | dimensionless | Bohr magneton number     | of a phase                                                                                     |

**Notes:** Suffixes may be used to some intensive variables and all extensive variables, as described below.

1) **Normalizing suffixes** \( \mathbf{M}, \mathbf{W}, \) and \( \mathbf{V} \) **for energetic extensive variables of a system:**

Normalizing suffixes like \( \mathbf{M} \) (per mole), \( \mathbf{W} \) (per mass in gram) or \( \mathbf{V} \) (per volume in \( \text{m}^3 \)) of the whole system (including all the components) can be supplied on all following energetic extensive variables for the system:

\[
Z = G, A, U, H, S, V \quad \Rightarrow \quad 2M, 2W, 2V
\]

Such suffixed quantities are calculated via the first derivatives of the energetic extensive variable \( Z \) with respect to \( N \) or \( B \) or \( V \) in the whole system. For instance,

\[
\begin{align*}
\mathbf{G}M &= \frac{\partial G}{\partial N} \\
\mathbf{G}W &= \frac{\partial G}{\partial B} \\
\mathbf{G}V &= \frac{\partial G}{\partial V}
\end{align*}
\]

Gibbs energy per mole of the system (J/mol)

Gibbs energy per mass of the system (J/g)

Gibbs energy per volume of the system (J/m^3)

Note that \( \mathbf{V}V \) is always as unit so it is unnecessary to evaluate such a quantity in the program.

2) **Normalizing suffixes** \( \mathbf{M}, \mathbf{W}, \mathbf{V} \) and \( \mathbf{F} \) **for energetic extensive variables of a phase:**

Normalizing suffixes like \( \mathbf{M} \) (per mole), \( \mathbf{W} \) (per mass in gram), \( \mathbf{V} \) (per volume in \( \text{m}^3 \)) or \( \mathbf{F} \) (per mole formula unit) of a phase can be supplied on all following energetic extensive variables for the phase:

\[
Z = G(\text{ph}), A(\text{ph}), U(\text{ph}), H(\text{ph}), S(\text{ph}), V(\text{ph}) \quad \Rightarrow \quad 2M, 2W, 2V, 2F
\]

Such suffixed quantities are calculated via the first derivatives of the energetic extensive variable \( Z \) with respect to \( \text{NP}(\text{ph}) \) or \( \text{BP}(\text{ph}) \) or \( \text{VP}(\text{ph}) \) for the phase. For instance,

\[
\begin{align*}
\mathbf{G}M(\text{ph}) &= \frac{\partial G(\text{ph})}{\partial \text{NP}(\text{ph})} \\
\mathbf{G}W(\text{ph}) &= \frac{\partial G(\text{ph})}{\partial \text{BP}(\text{ph})} \\
\mathbf{G}V(\text{ph}) &= \frac{\partial G(\text{ph})}{\partial \text{VP}(\text{ph})} \\
\mathbf{G}F(\text{ph}) &= \frac{\partial G(\text{ph})}{\partial \text{NP}(\text{ph})} \times \text{NA}
\end{align*}
\]

Gibbs energy of the phase per mole of the phase (J/mol)

Gibbs energy of the phase per mole of the phase (J/mol)

Gibbs energy of the phase per volume of the phase (J/mol)

Gibbs energy of the phase per formula unit of the phase (J/mol)

(\text{where NA stands for total atomic number in the phase formula})

One shall note that: if a phase is unstable in the system, and thus its \( \text{NP}(\text{ph}), \text{BP}(\text{ph}) \) and \( \text{VP}(\text{ph}) \) values equal to zero, \( G(\text{ph}), A(\text{ph}), U(\text{ph}), H(\text{ph}), S(\text{ph}) \) and \( V(\text{ph}) \) are all assigned with zero value. However, \( \mathbf{G}M(\text{ph}), \mathbf{AM}(\text{ph}), \mathbf{UM}(\text{ph}), \mathbf{HM}(\text{ph}), \mathbf{SM}(\text{ph}) \) and \( \mathbf{VM}(\text{ph}) \), as well as all the \( \mathbf{W}/V/F \)-suffixed quantities are precisely calculated and stored in the workspaces, according to the thermodynamic model used for the phase, using the first derivatives of the Gibbs energy expressed for the phase with respect to the current composition in the system.

Also note that \( \mathbf{V}V(\text{ph}) \) is always as unity so it is unnecessary to evaluate such a quantity in the program.

3) **Normalizing suffixes** \( \mathbf{M}, \mathbf{W}, \mathbf{V} \) and \( \mathbf{F} \) **for the energetic extensive variable** \( DG \) **of a phase:**

Normalizing suffixes like \( \mathbf{M} \) (per mole), \( \mathbf{W} \) (per mass in gram), \( \mathbf{V} \) (per volume in \( \text{m}^3 \)) or \( \mathbf{F} \) (per mole formula unit) of a phase must always be supplied on the energetic extensive variable \( DG \) for the phase:

\[
Z = DG(\text{ph}) \quad \Rightarrow \quad 2M, 2W, 2V, 2F \quad \text{(Note this can not be used as conditions)}
\]

Theoretically, such suffixed quantities can calculated via the first derivatives of the energetic extensive variable \( DG(\text{ph}) \) with respect to \( \text{NP}(\text{ph}) \) or \( \text{BP}(\text{ph}) \) or \( \text{VP}(\text{ph}) \) for the phase. For instance,

\[
\begin{align*}
\mathbf{DG}M(\text{ph}) &= \frac{\partial DG(\text{ph})}{\partial \text{NP}(\text{ph})} \\
\mathbf{DG}W(\text{ph}) &= \frac{\partial DG(\text{ph})}{\partial \text{BP}(\text{ph})} \\
\mathbf{DG}V(\text{ph}) &= \frac{\partial DG(\text{ph})}{\partial \text{VP}(\text{ph})} \\
\mathbf{DG}F(\text{ph}) &= \frac{\partial DG(\text{ph})}{\partial \text{NP}(\text{ph})} \times \text{NA}
\end{align*}
\]

Driving force of the phase per mole of the phase (J/mol)

Driving force of the phase per mass of the phase (J/mol)

Driving force of the phase per volume of the phase (J/mol)

Driving force of the phase per formula unit of the phase (J/mol)
Thermo-Calc State Variables & Derived Variables

However, please note that the \( \Delta G(\text{ph}) \) is never directly calculated in the program, and thus the above four quantities are not calculated followed these equations. Instead, these driving force quantities for a specific phase are calculated precisely using the second derivatives of the Gibbs energy expressed for the phase with respect to the current compositions in the equilibrium state of the system.

4) Normalizing suffixes \( M \), \( W \) and \( V \) for compositional extensive variables of a system:

Normalizing suffixes like \( M \) (per mole), \( W \) (per mass in gram) or \( V \) (per volume in m\(^3\)) of the whole system (including all system components) can be supplied on all following compositional extensive variables for the system:

\[
Z = N, \ B \quad \rightarrow \quad 2M, \ 2W, \ 2V
\]

Such suffixed quantities are calculated via the first derivatives of the compositional extensive variable \( Z \) with respect to \( N \) or \( B \) or \( V \) in the whole system. For instance,

\[
\begin{align*}
NW &= \frac{\partial N}{\partial B} & \text{Mole number of components per mass of the system (mol/g)} \\
NV &= \frac{\partial N}{\partial V} & \text{Mole number of components per volume of the system (mol/m}^3\text{)} \\
BM &= \frac{\partial B}{\partial N} & \text{Mass (gram) of components per mole of the system (g/mol)} \\
BV &= \frac{\partial B}{\partial V} & \text{Mass (gram) of components per volume of the system (g/m}^3\text{)}
\end{align*}
\]

Note that the followings:
- \( NM \) and \( BW \) for overall amount (size) of the system are always as unity (so it is unnecessary to evaluate them);
- \( BW \) and \( BM \) cannot be set as conditions;
- \( BV \) is the density of the entire system

5) Normalizing suffixes \( M \), \( W \) and \( V \) for compositional extensive variables a component in the system:

Normalizing suffixes like \( M \) (per mole), \( W \) (per mass in gram) or \( V \) (per volume in m\(^3\)) of the whole system (including all system components) can be supplied on all following compositional extensive variables for a component in the system:

\[
Z = N(\text{comp}), \ B(\text{comp}) \quad \rightarrow \quad 2M, \ 2W, \ 2V
\]

Such suffixed quantities are calculated via the first derivatives of the compositional extensive variable \( Z \) with respect to \( N \) or \( B \) or \( V \) in the whole system. For instance,

\[
\begin{align*}
NM(\text{comp}) &= \frac{\partial N(\text{comp})}{\partial N} & \text{Mole number of a component per mole of the system (mole fraction)} \\
NW(\text{comp}) &= \frac{\partial N(\text{comp})}{\partial B} & \text{Mole number of a component per mass of the system (mol/g)} \\
NV(\text{comp}) &= \frac{\partial N(\text{comp})}{\partial V} & \text{Mole number of a component per volume of the system (mol/m}^3\text{)} \\
BM(\text{comp}) &= \frac{\partial B(\text{comp})}{\partial N} & \text{Mass (gram) of a component per mole of the system (g/mol)} \\
BW(\text{comp}) &= \frac{\partial B(\text{comp})}{\partial B} & \text{Mass (gram) of a component per mass of the system (mass fraction)} \\
BV(\text{comp}) &= \frac{\partial B(\text{comp})}{\partial V} & \text{Mass (gram) of a component per volume of the system (g/m}^3\text{)}
\end{align*}
\]

Note that some suffixed extensive variables stand for certain special quantities, as listed below:
- \( NM(\text{comp}) = X(\text{comp}) \) for mole fraction of a component in the system;
- \( BW(\text{comp}) = W(\text{comp}) \) for mass fraction of a component in the system.

6) Normalizing suffixes \( M \), \( W \) and \( V \) for compositional extensive variables of a phase in the system:

Normalizing suffixes like \( M \) (per mole), \( W \) (per mass in gram) or \( V \) (per volume in m\(^3\)) of the whole system (including all system components) can be supplied on compositional extensive variables \( NF(\text{ph}) \) and \( BP(\text{ph}) \) [as well as the \( VP(\text{ph}) \) quantity] for a phase:

\[
Z = NF(\text{ph}), \ BP(\text{ph}), \ VP(\text{ph}) \quad \rightarrow \quad 2M, \ 2W, \ 2V
\]

Such suffixed quantities are calculated via the first derivatives of such extensive variable \( Z \) with respect to \( N \) or \( B \) or \( V \) in the whole system. For instance,

\[
\begin{align*}
NPM(\text{ph}) &= \frac{\partial NF(\text{ph})}{\partial N} & \text{Mole number of a phase per mole of the system (mole fraction)} \\
NPW(\text{ph}) &= \frac{\partial NF(\text{ph})}{\partial B} & \text{Mole number of a phase per mass of the system (mol/g)} \\
NPV(\text{ph}) &= \frac{\partial NF(\text{ph})}{\partial V} & \text{Mole number of a phase per volume of the system (mol/m}^3\text{)} \\
BPM(\text{ph}) &= \frac{\partial BP(\text{ph})}{\partial N} & \text{Mass (gram) of a phase per mole of the system (g/mol)} \\
BPW(\text{ph}) &= \frac{\partial BP(\text{ph})}{\partial B} & \text{Mass (gram) of a phase per mass of the system (mass fraction)} \\
BPV(\text{ph}) &= \frac{\partial BP(\text{ph})}{\partial V} & \text{Mass (gram) of a phase per volume of the system (g/m}^3\text{)} \\
VPM(\text{ph}) &= \frac{\partial VP(\text{ph})}{\partial N} & \text{Volume (m}^3\text{) of a phase per mole of the system (m}^3\text{/mol)} \\
VPW(\text{ph}) &= \frac{\partial VP(\text{ph})}{\partial B} & \text{Volume (m}^3\text{) of a phase per mass of the system (m}^3\text{/g)} \\
VPV(\text{ph}) &= \frac{\partial VP(\text{ph})}{\partial V} & \text{Volume (m}^3\text{) of a phase per volume of the system (volume fraction)}
\end{align*}
\]

Note that the \( VP(\text{ph}) \) variable is exactly the \( V(\text{ph}) \) property, but their \( M/W/V/F \)-suffixed quantities are different; \( VP(\text{ph}) \) can be \( V \)-suffixed (but not \( F \)-suffixed) while \( V(\text{ph}) \) can be \( F \)-suffixed (but not \( V \)-suffixed).
Also note that: if a phase is unstable in the equilibrium system, the \( NP(\text{ph}) \), \( BP(\text{ph}) \) and \( VP(\text{ph}) \) values equals to zero, and do so their M/W/V-suffixed quantities.

One should also keep in mind that: the phase amount variables, \( NP(\text{ph}) \), \( BP(\text{ph}) \) and \( VP(\text{ph}) \), as well as all their M/W/V-suffixed quantities, should not be used as conditions. Instead, one can change the status of a phase to FIXED and set the molar amount.

7) Normalizing suffixes \( M \), \( W \) and \( V \) for compositional extensive variables of a component in a phase:

Normalizing suffixes like \( M \) (per mole), \( W \) (per mass in gram) or \( V \) (per volume in \( m^3 \)) of a phase can be supplied on all following compositional extensive variables for a component in the phase:

\[
Z = N(\text{ph,comp}), \ B(\text{ph,comp}) \quad \rightarrow \quad ZM, \ ZW, \ ZV
\]

Such suffixed quantities are calculated via the first derivatives of the compositional extensive variable \( Z \) with respect to \( N \) or \( B \) or \( V \) in the whole system. For instance,

\[
NM(\text{ph,comp}) = \frac{\partial N(\text{ph,comp})}{\partial NP(\text{ph})} \quad \text{Mole number of a component per mole of a phase (mole fraction)}
\]

\[
NW(\text{ph,comp}) = \frac{\partial N(\text{ph,comp})}{\partial BP(\text{ph})} \quad \text{Mole number of a component per mass of a phase (mol/g)}
\]

\[
NV(\text{ph,comp}) = \frac{\partial N(\text{ph,comp})}{\partial VP(\text{ph})} \quad \text{Mole number of a component per volume of a phase (mol/m^3)}
\]

\[
BM(\text{ph,comp}) = \frac{\partial B(\text{ph,comp})}{\partial NP(\text{ph})} \quad \text{Mass (gram) of a component per mole of a phase (g/mol)}
\]

\[
BW(\text{ph,comp}) = \frac{\partial B(\text{ph,comp})}{\partial BP(\text{ph})} \quad \text{Mass (gram) of a component per mass of a phase (g/mol)}
\]

\[
BV(\text{ph,comp}) = \frac{\partial B(\text{ph,comp})}{\partial VP(\text{ph})} \quad \text{Mass (gram) of a component per volume of a phase (g/m^3)}
\]

Note that some suffixed extensive variables stand for certain special quantities, as listed below:

\[
\begin{align*}
\text{NM}(\text{ph,comp}) &= X(\text{ph,comp}) \quad \text{for mole fraction of a component in a phase;}
\text{BW}(\text{ph,comp}) &= W(\text{ph,comp}) \quad \text{for mass fraction of a component in a phase;}
\end{align*}
\]

8) Special compositional (extensive) variables of a component or a species:

The derived compositional variables, \( X\% (\text{comp}) \) and \( W\% (\text{comp}) \) for a system component, as well as \( IN(sp) \) and \( IM(sp) \) for a species (phase constituent), are only available in the TQ and TCAPI programming interfaces.

However, the quantities with the meaning of \( X\% (\text{comp}) \) and \( W\% (\text{comp}) \) can be used as axis variables in diagrams but they must be specified as the followings, respectively:

\[
\begin{align*}
\text{Mole-Percent} & \ <\text{comp}> \quad \text{for mole-percent of a component in the system, } X(\text{comp});
\text{Weight-Percent} & \ <\text{comp}> \quad \text{for mass-percent of a component in the system, } W(\text{comp}).
\end{align*}
\]

Note that neither of these variables or relevant syntaxes can be used as conditions for the system.

Moreover, when plotting mole-fraction or mass-fraction of a component in the system as a diagram axis, it is recommended to use the following syntaxes, respectively:

\[
\begin{align*}
\text{Mole-Fraction} & \ <\text{comp}> \quad \text{for mole-fraction of a component in the system, } X(\text{comp});
\text{Weight-Fraction} & \ <\text{comp}> \quad \text{for mass-fraction of a component in the system, } W(\text{comp}).
\end{align*}
\]

rather than directly using their relevant state variables, \( X(\text{comp}) \) or \( W(\text{comp}) \).

9) Special quantity \( QF \) of a phase:

The Thermo-Calc software system also calculates a special quantity, the \textit{phase stability function} \( QF(\text{ph}) \), for all kinds of phases in an equilibrium state. A phase stability function for a phase is negative when the phase composition is inside a spinodal, or positive elsewhere. Like an intensive variable, it cannot have any normalization suffix (\( M \), \( W \), \( V \) or \( F \)). This special quantity cannot be used as a condition.

It is very useful for finding out if a calculated equilibrium state is possibly within the miscibility gap for a solution phase.

10) Special quantities \( TC \) and \( BMAGN \) of a phase with magnetic contribution:

The Thermo-Calc software system also calculates other two special quantities, the \textit{Curie temperature} \( TC(\text{ph}) \) and \textit{Bohr magneton number} \( BMAGN(\text{ph}) \), for all kinds of phases possibly with magnetic contributions in an equilibrium state. Such a quantity is calculated using a certain model to handle magnetic contributions \( e.g. \), the Inden’s Model for treating pure ferro-/antiferro-/para-magnetic phases, and for modelling solution phases with magnetic ordering/transformations where Curie temperature and Bohr magneton number are dependent upon the composition of the phase). These two special quantities cannot be used as conditions.

11) Reference State suffix \( R \) for state variables of a system or a component or a phase or a constituent:
The so-called reference state suffix $R$ can be added on intensive variables $MU$, $AC$, or $LNAC$ in order to get a value that is calculated with respect to a chosen reference state, e.g., $MUR(comp)$, $ACR(comp)$ and $LNACR(comp)$ for a components in the system, and $MUR(sp, ph)$, $ACR(sp, ph)$ and $LNACR(sp, ph)$ for a species in a specific solution phase.

When the reference state for a system component is the default reference state (usually the SER – Stable Reference State, SER to “GRAPHITE * 1E5”) in the Fe-Cr-Ni-C-O system, one will notice the following unequal relations:

- $MUR(comp)=MU(comp)$
- $ACR(comp)=AC(comp)$
- $LNACR(comp)=LNAC(comp)$

However, if another reference state has been set for a system component the above relations do not hold true any longer.

The chemical potentials and activities of species in some single-sublattice solution phases (such as aqueous solution, gaseous mixture, metallic liquid solution, slag mixture, MO solid solution, etc.) are specially-treated state variables, denoted as $MU(sp, ph)$, $MUR(sp, ph)$, $AC(sp, ph)$, $ACR(sp, ph)$, $LNAC(sp, ph)$ and $LNACR(sp, ph)$. For some such solution phases in their specific databases (e.g., AQUEOUS solution phase in the TCAQ or AQS databases, FE_LIQUID solution phase in the SLAG database), the reference states and standard states of various solution species have been properly pre-defined by their corresponding thermodynamic models. Please keep in mind that for all solution species treated by any solution model in any database, there are always the relations: $MUR(sp, ph)=MU(sp, ph)$, $ACR(sp, ph)=AC(sp, ph)$, and $LNACR(sp, ph)=LNAC(sp, ph)$.

The suffix $R$ can also be added on the special variables $QF(ph)$, $TC(ph)$ and $BMAGN(ph)$, but a $R$-suffixed quantity is always identical to its original variable, e.g., $QFR(ph)=QF(ph)$, under a specific condition in a defined system. In other words, the phase stability functions, Curie temperature and Bohr magneton number of various phases do not change along the so-called stable reference state suffix $R$-suffixed variables of an entire system, of a component, of a phase, or of a phase constituent, however, one should first understand the meaning of such $R$-suffixed state variables before using them. An $R$-suffixed compositional variable is always identical to its original variable (implying that the suffix $R$ may not make any different on a compositional variable), e.g.

- $NR = N$
- $NMR(comp)=NM(comp)=X(comp)$
- $NPR(ph)=NP(ph)$
- $YR(ph, cons#sub)=Y(ph, cons#sub)$

Total size (moles of all components) of the whole system
Mole fraction of a component in the whole system
Mole number of a phase
Site fractions of a constituent on a site in a phase

On the contrary, an $R$-suffixed energetic variable (for the whole system or for a phase) may differ from its original state variable, depending upon the setting of reference states for all components in the defined system. The general expressions for calculating $R$-suffixed energetic state variable are as follows:

$$ZR = Z – X(comp)\sum_{i=1}^{n} Z(comp)^{REF}$$

(for the whole system)

$$ZR(ph) = Z(ph) – X(ph, comp)\sum_{i=1}^{n} Z(comp)^{REF}$$

(for a phase)

For instance, after the redefinition of the reference state of the system component C (changed from SER to “GRAPHITE * 1E5”) in the Fe-Cr-Ni-C-O system, one will notice the following unequal relations:

- $GR \neq G$
- $GRM \neq GM$
- $HWR \neq HW$
- $SVR \neq SV$
- $GR(ph) \neq G(ph)$
- $GVR(ph) \neq GV(ph)$
- $HMR(ph) \neq HM(ph)$
- $SWR(ph) \neq SW(ph)$

12) **Heat capacity of a system or a phase:**

Heat capacity (at constant pressure or volume) of a system or of a specific phase in the system are partial derivatives of state variable enthalpy with respect to temperature, by using the dot "." notation between the two state variables (see more descriptions in Section 2, Derived variables):

- $HM, T = \partial HM / \partial T$
  
  heat capacity for the system at either constant $P$ (if pressure is a condition)
  
  or constant $V$ (if volume is a condition)

- $HM(ph). T = \partial HM (ph) / \partial T$
  
  heat capacity for a phase at either constant $P$ (if pressure is a condition)
  
  or constant $V$ (if volume is a condition)
2 Derived Variables (Partial Derivatives)

The state variables can be used to define additional functions or variables, through some mathematical expressions of state variables or other functions. Such functions or variables are referred as partial derivatives or derived variables.

Actually, some variables listed in Table 1 are derived variables, e.g., $HM.T$ and $HM.(ph).T$, where a dot “.” notation is used. As an important feature of the Thermo-Calc software, any partial derivatives of one state variable with respect to another can be evaluated, by using the dot “.” notation between the two state variables. However, the state variable after the dot must be set as a condition. For example,

\[
HM.T = (\partial HM/\partial T)_{\text{condition}} \quad \text{heat capacity for the system at either constant } P, C_p \text{ (if pressure is a condition)} \\
\text{or constant } V, C_v \text{ (if volume is a condition)}
\]

\[
HM.(ph).T = (\partial HM.(ph)/\partial T)_{\text{condition}} \quad \text{heat capacity for a phase at either constant } P, C_p.(ph) \text{ (if pressure is a condition)} \\
\text{or constant } V, C_v.(ph) \text{ (if volume is a condition)}
\]

\[
H.T = \partial H/\partial T \quad \text{heat capacity for the system multiplied by total mole number of components} \\
i.e., \partial H/\partial T = C_p*N \quad \text{(if pressure is a condition in a close system)} \\
\partial H/\partial T = C_v*N \quad \text{(if volume is a condition in a close system)}
\]

\[
H.(ph).T = \partial H.(ph)/\partial T \quad \text{heat capacity for a phase multiplied by } NP.(ph) \text{ plus } HM.(ph)\partial VM.(ph)/\partial T \\
i.e., C_p.(ph)*NP.(ph) + HM.(ph)\partial VM.(ph)/\partial T \quad \text{(if pressure is a condition)} \\
C_v.(ph)*NP.(ph) + HM.(ph)\partial VM.(ph)/\partial T \quad \text{(if volume is a condition)}
\]

\[
VM.T = \partial VM/\partial T \quad \text{thermal expansivity of the system (already multiplied by the total molar volume) } \\
i.e., \partial VM/\partial T = \alpha*VM
\]

\[
VM.(ph).T = \partial VM.(ph)/\partial T \quad \text{thermal expansivity of a phase (already multiplied by its molar volume) } \\
i.e., \partial VM.(ph)/\partial T = \alpha.(ph)*VM.(ph)
\]

\[
V.T = \partial V/\partial T \quad \text{thermal expansivity of the system (already multiplied by the total volume) } \\
i.e., \partial V/\partial T = \alpha*V
\]

\[
V.(ph).T = \partial V.(ph)/\partial T \quad \text{thermal expansivity of a phase (already multiplied by the phase volume) } \\
i.e., \partial V.(ph)/\partial T = \alpha.(ph)*V.(ph)
\]

\[
VM.(ph).P = -\partial VM.(ph)/\partial P \quad \text{isothermal compressibility of the system (already multiplied by the total molar volume) } \\
i.e., \partial VM.(ph)/\partial P = -\kappa*VM
\]

\[
VM.(ph).P = -\partial VM.(ph)/\partial P \quad \text{isothermal compressibility of a phase (already multiplied by its molar volume) } \\
i.e., \partial VM.(ph)/\partial P = -\kappa.(ph)*VM.(ph)
\]

\[
V.(ph).P = -\partial V.(ph)/\partial P \quad \text{isothermal compressibility of the system (already multiplied by the total volume) } \\
i.e., \partial V.(ph)/\partial P = -\kappa*V
\]

\[
V.(ph).P = -\partial V.(ph)/\partial P \quad \text{isothermal compressibility of a phase (already multiplied by the phase volume) } \\
i.e., \partial V.(ph)/\partial P = -\kappa*V.(ph)
\]

\[
T.X.(comp) = \partial T/\partial X.(comp) \quad \text{slope of a phase boundary on a } T-X.(comp) \text{ phase diagram with respect to mole fraction of the component in the system}
\]

\[
T.W.(comp) = \partial T/\partial W.(comp) \quad \text{slope of a phase boundary on a } T-W.(comp) \text{ phase diagram with respect to mass of the component in the system}
\]

\[
T.X.(ph,comp) = \partial T/\partial X.(ph,comp) \quad \text{slope of a phase boundary on a } T-X.(ph,comp) \text{ phase diagram with respect to mole fraction of the component in the phase}
\]

\[
T.W.(ph,comp) = \partial T/\partial W.(ph,comp) \quad \text{slope of a phase boundary on a } T-W.(ph,comp) \text{ phase diagram with respect to mole fraction of the component in the phase}
\]

\[
P.T = \partial P/\partial T \quad \text{slope of a phase boundary on a } P-T \text{ phase diagram (Note that the equilibrium with phase assemblage must be calculated first)}
\]

Restrictedly speaking, those energetic extensive variables with normalizing suffixes like $M$ (per mole of component), $W$ (per mass in gram), $V$ (per volume in m$^3$) or $F$ (per mole formula unit) of the entire system, or a specific phase, as listed in Table 1, are derived variables, which have been explicitly defined inside the program by using expressions as either first or second derivatives of some state variables with respect to other independent state variables. Therefore, the derived variable $G.B$ is exactly the same as the $W$-suffixed state variable $GW$ when $B$ (total mass of all components in the system) has been defined as an equilibrium condition in the system. In case a phase is not stable in the system, such derived quantities for the phase will be still precisely calculated by the program and saved in the workspace. See the comments below the table.
Moreover, those compositional extensive variables with normalizing suffixes like \( M \) (per mole), \( \mathcal{W} \) (per mass in gram), \( V \) (per volume in \( m^3 \)), \( F \) (per mole formula unit), or \( \% \) (percent) of the entire system, any specific or all system components in the whole system, or a given phase, or any specific or all system components in a given phase, as listed in Table 1, are also derived variables, which are defined by expressions of some independent state variables. Therefore, the derived variable \( N(\text{comp}).N \) is exactly the same as the \( M \)-suffixed state variable \( N(\text{comp}) \) or \( X(\text{comp}) \) when \( N \) (total moles of all components in the system) has been defined as an equilibrium condition in the system. For instance,

\[
\begin{align*}
N.N &= \frac{\partial N}{\partial N} \\
N.B &= \frac{\partial N}{\partial B} \\
N.V &= \frac{\partial N}{\partial V} \\
B.N &= \frac{\partial B}{\partial N} \\
B.B &= \frac{\partial B}{\partial B} \\
B.V &= \frac{\partial B}{\partial V} \\
\end{align*}
\]

\( (always \ as \ unity \ so \ it \ is \ unnecessary:) \)

\[
\begin{align*}
N(\text{comp}).N &= \frac{\partial N(\text{comp})}{\partial N} \\
N(\text{ph},\text{comp}).N &= \frac{\partial N(\text{ph},\text{comp})}{\partial N} \\
B(\text{comp}).B &= \frac{\partial B(\text{comp})}{\partial B} \\
B(\text{ph},\text{comp}).B &= \frac{\partial B(\text{ph},\text{comp})}{\partial B} \\
W(\text{comp}) &= \frac{\partial W(\text{comp})}{\partial W} \\
\end{align*}
\]

\( (always \ as \ unity \ so \ it \ is \ unnecessary:) \)

\[
\begin{align*}
N(\text{comp}).N &= X(\text{comp}) \\
N(\text{ph},\text{comp}).N &= X(\text{ph},\text{comp}) \\
N(\text{ph}).N &= X(\text{ph}) \\
B(\text{comp}).B &= B(\text{comp}) \\
B(\text{ph},\text{comp}).B &= B(\text{ph},\text{comp}) \\
W(\text{comp}) &= W(\text{comp}) \\
\end{align*}
\]