

**UNIVERSIDADE DE SÃO PAULO – USP
ESCOLA DE ENGENHARIA DE LORENA – EEL
DEPARTAMENTO DE ENGENHARIA DE MATERIAIS – DEMAR**

Termodinâmica Computacional – Descrição Básica

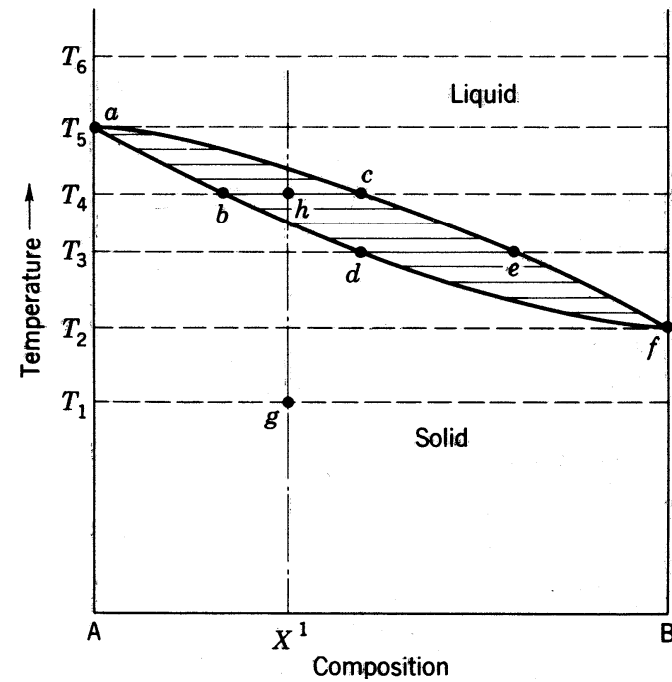
**Gilberto Carvalho Coelho
DEMAR–EEL–USP, Lorena, São Paulo**

Roteiro

- **Termodinâmica Computacional**
- **Desenvolvimento de Banco de Dados**
- **Aplicação da Termodinâmica Computacional**

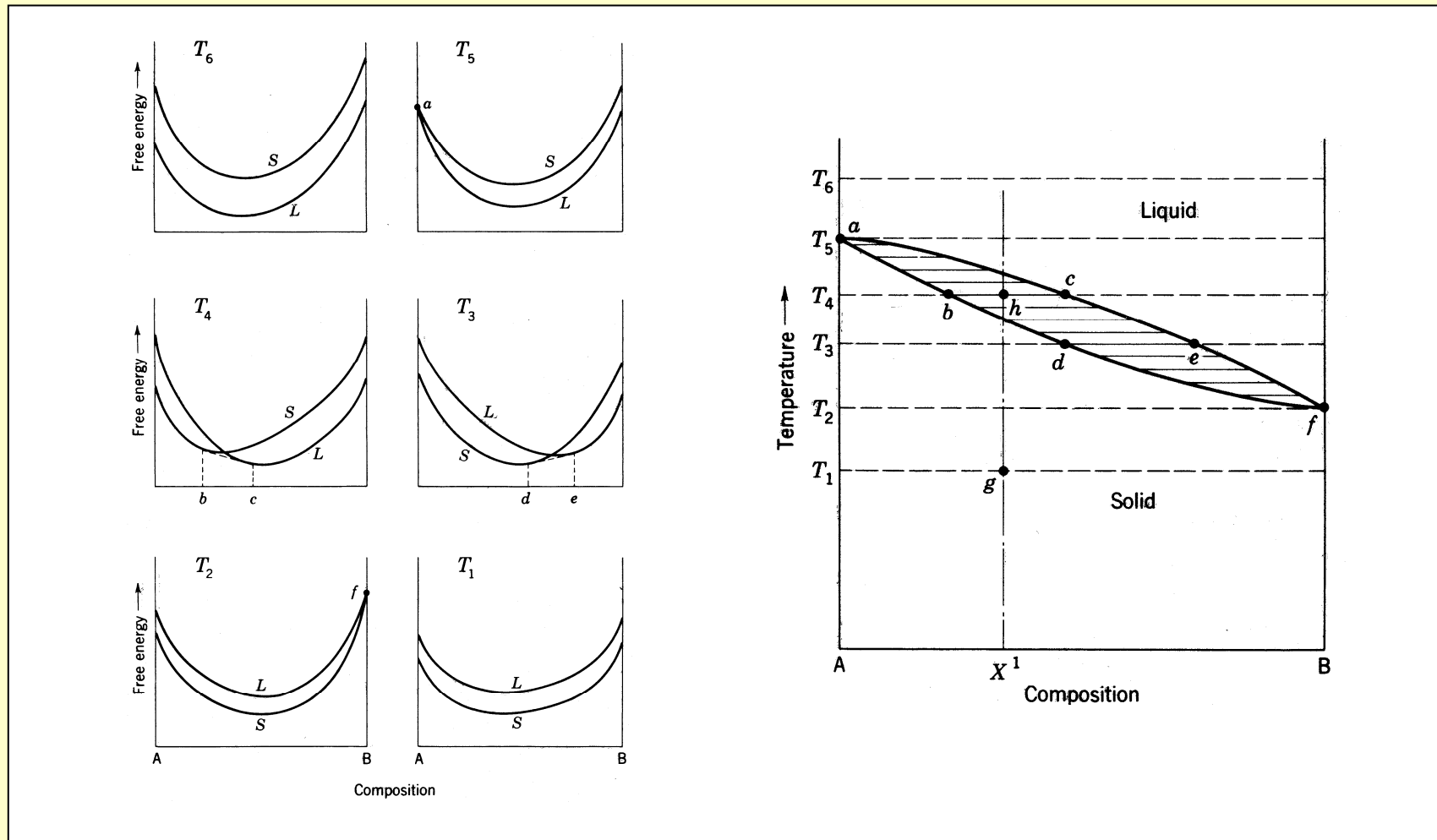
Termodinâmica Computacional

Termodinâmica e Diagrama de Fases



Termodinâmica Computacional

Termodinâmica e Diagrama de Fases

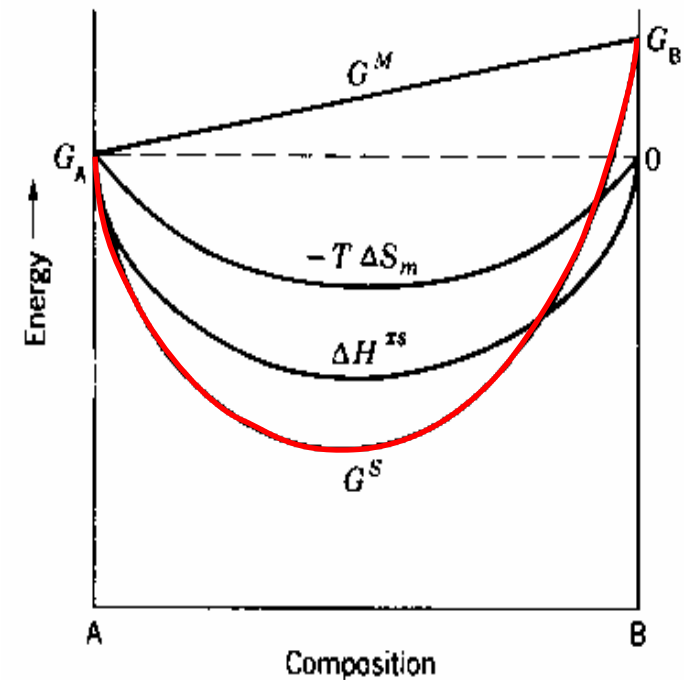


Termodinâmica Computacional

CALPHAD (CALculation of PHase Diagram)

- Dependência da Composição

➤ $G^\phi - H^{\text{SER}} = {}^{\text{ref}}G + {}^{\text{id}}G^\phi + {}^{\text{E}}G^\phi$

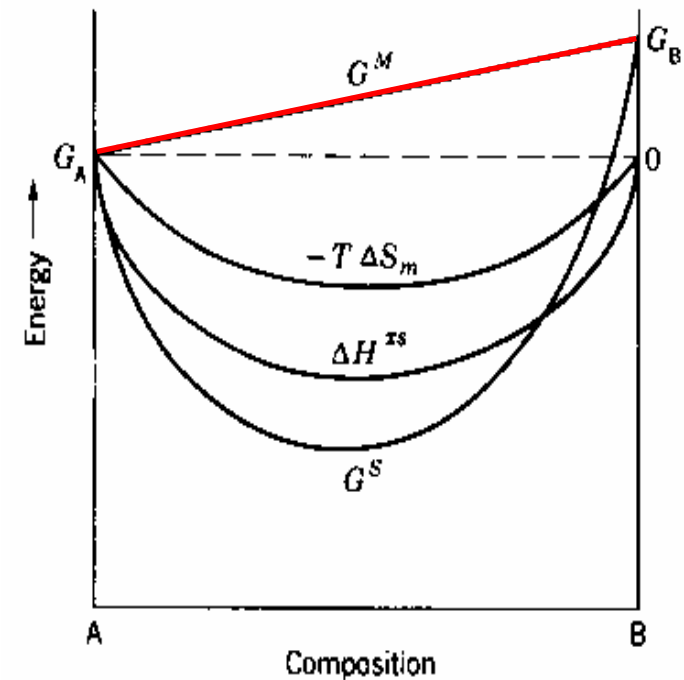


Termodinâmica Computacional

CALPHAD (CALculation of PHase Diagram)

- Dependência da Composição

- $G^\phi - H^{\text{SER}} = \text{ref}G + \text{id}G^\phi + E G^\phi$
- $\text{ref}G = [{}^0G_i^{\text{ref1}}(T) - H_i^{\text{SER}}(298,15\text{K})] \cdot x_i + [{}^0G_j^{\text{ref2}}(T) - H_j^{\text{SER}}(298,15\text{K})] \cdot x_j$

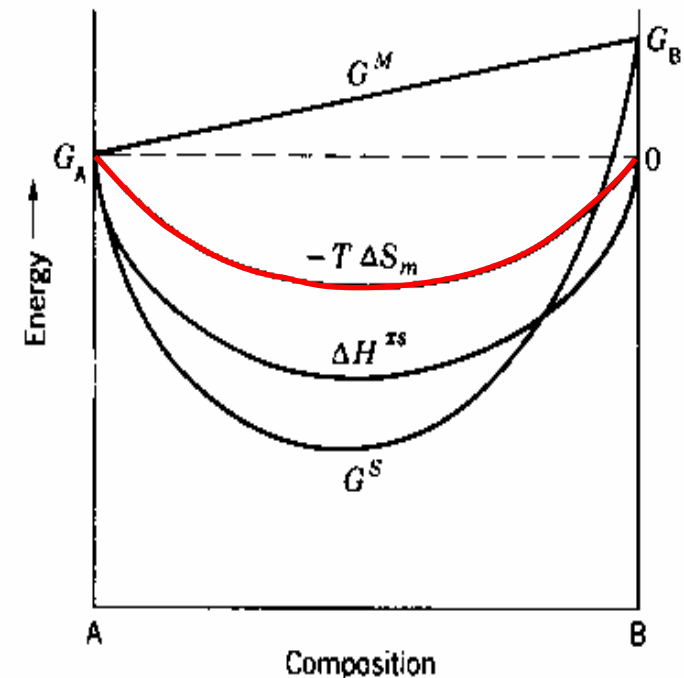


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CALPHAD (CALculation of PHase Diagram)

- Dependência da Composição

- $G^\phi - H^{\text{SER}} = \text{ref}G + \text{id}G^\phi + \text{EG}^\phi$
- $\text{ref}G = [{}^{\circ}G_i^{\text{ref1}}(T) - H_i^{\text{SER}}(298,15\text{K})] \cdot x_i + [{}^{\circ}G_j^{\text{ref2}}(T) - H_j^{\text{SER}}(298,15\text{K})] \cdot x_j$
- $\text{id}G^\phi = R \cdot T \cdot [x_i \cdot \ln(x_i) + x_j \cdot \ln(x_j)]$

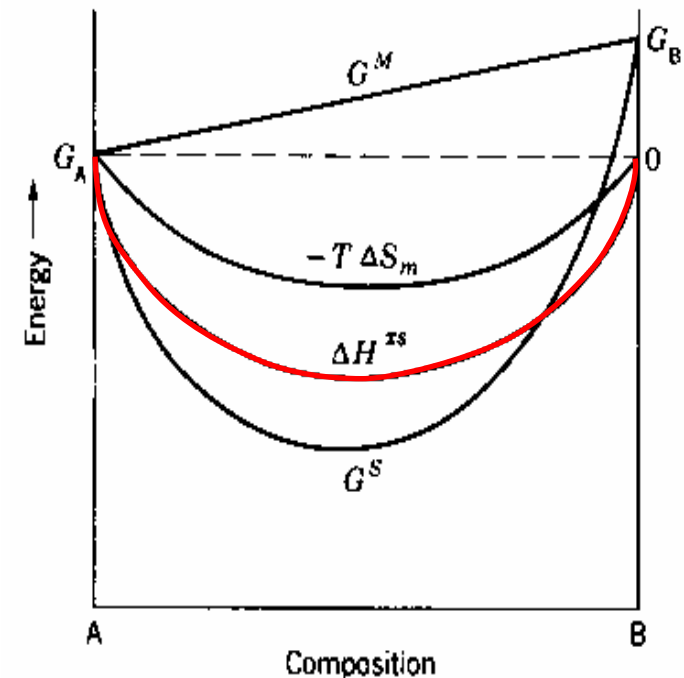


Termodinâmica Computacional

CALPHAD (CALculation of PHase Diagram)

• Dependência da Composição

- $G^\phi - H^{\text{SER}} = \text{ref}G + \text{id}G^\phi + \text{EG}^\phi$
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- $\text{id}G^\phi = R \cdot T \cdot [x_i \cdot \ln(x_i) + x_j \cdot \ln(x_j)]$
- $\text{EG}^\phi = x_i \cdot x_j \cdot [L_0 + L_1 \cdot (x_i - x_j) + \dots]$



Termodinâmica Computacional

CALPHAD (CALculation of PHase Diagram)

• Dependência da Composição

- $G^\phi - H^{\text{SER}} = {}^{\text{ref}}G + {}^{\text{id}}G^\phi + {}^{\text{E}}G^\phi$
- ${}^{\text{ref}}G = [{}^{\circ}G_i^{\text{ref1}}(T) - H_i^{\text{SER}}(298,15\text{K})] \cdot x_i + [{}^{\circ}G_j^{\text{ref2}}(T) - H_j^{\text{SER}}(298,15\text{K})] \cdot x_j$
- ${}^{\text{id}}G^\phi = R \cdot T \cdot [x_i \cdot \ln(x_i) + x_j \cdot \ln(x_j)]$
- ${}^{\text{E}}G^\phi = x_i \cdot x_j \cdot [L_0 + L_1 \cdot (x_i - x_j) + \dots]$

• Dependência da Temperatura

- ${}^{\circ}G_i - H_i^{\text{SER}} = A + B \cdot T + C \cdot T \cdot \ln(T) + \dots$

$$\Delta G_T = \Delta H_T - T \Delta S_T$$

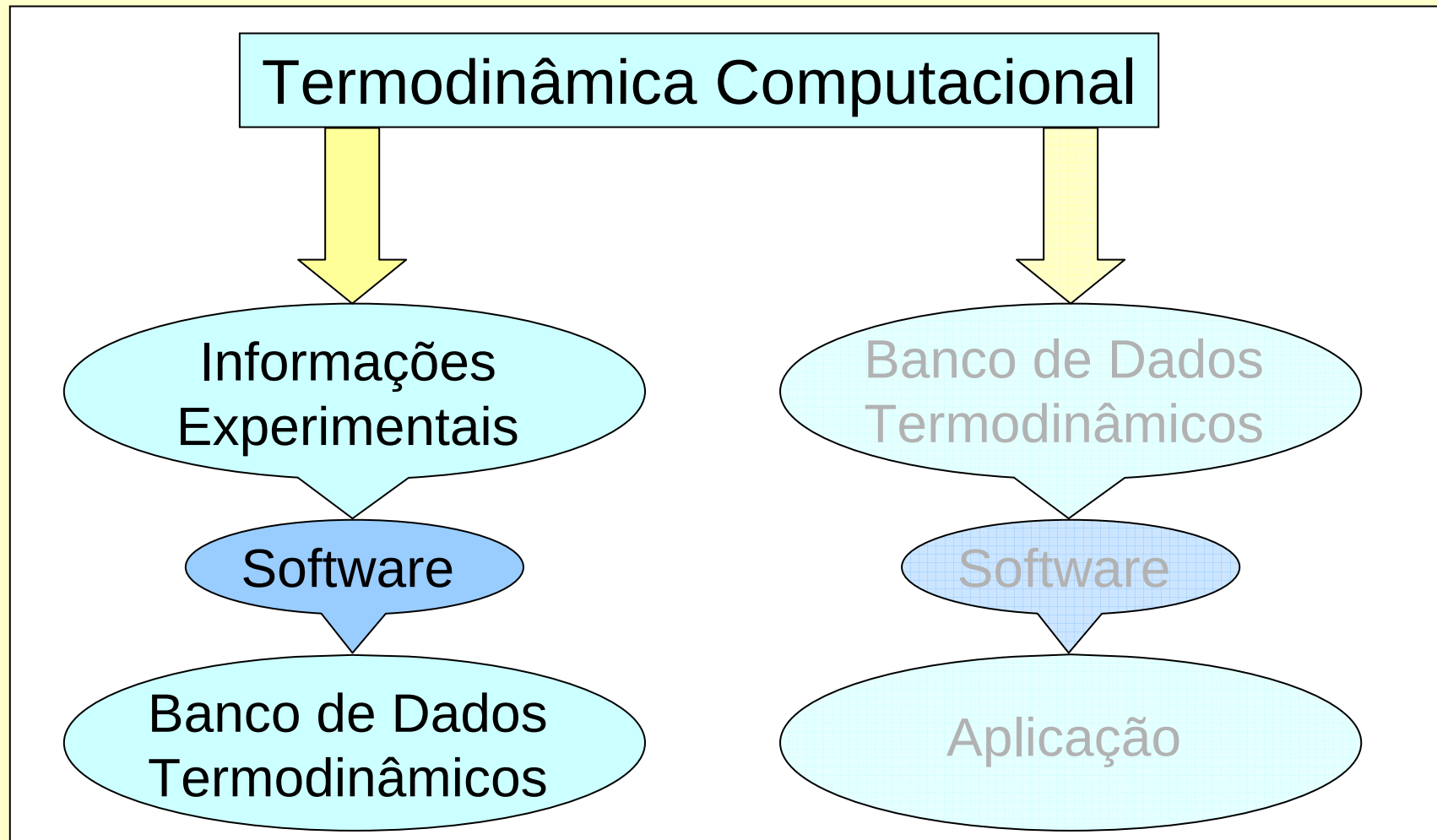
$$\Delta H_T = \Delta H_{298} + \int_{298}^T C_p dT$$

$$\Delta S_T = S_{298} + \int_{298}^T \frac{C_p}{T} dT$$

$$\Delta G_T = \Delta H_{298} - T S_{298} + \int_{298}^T C_p dT - T \int_{298}^T \frac{C_p}{T} dT$$

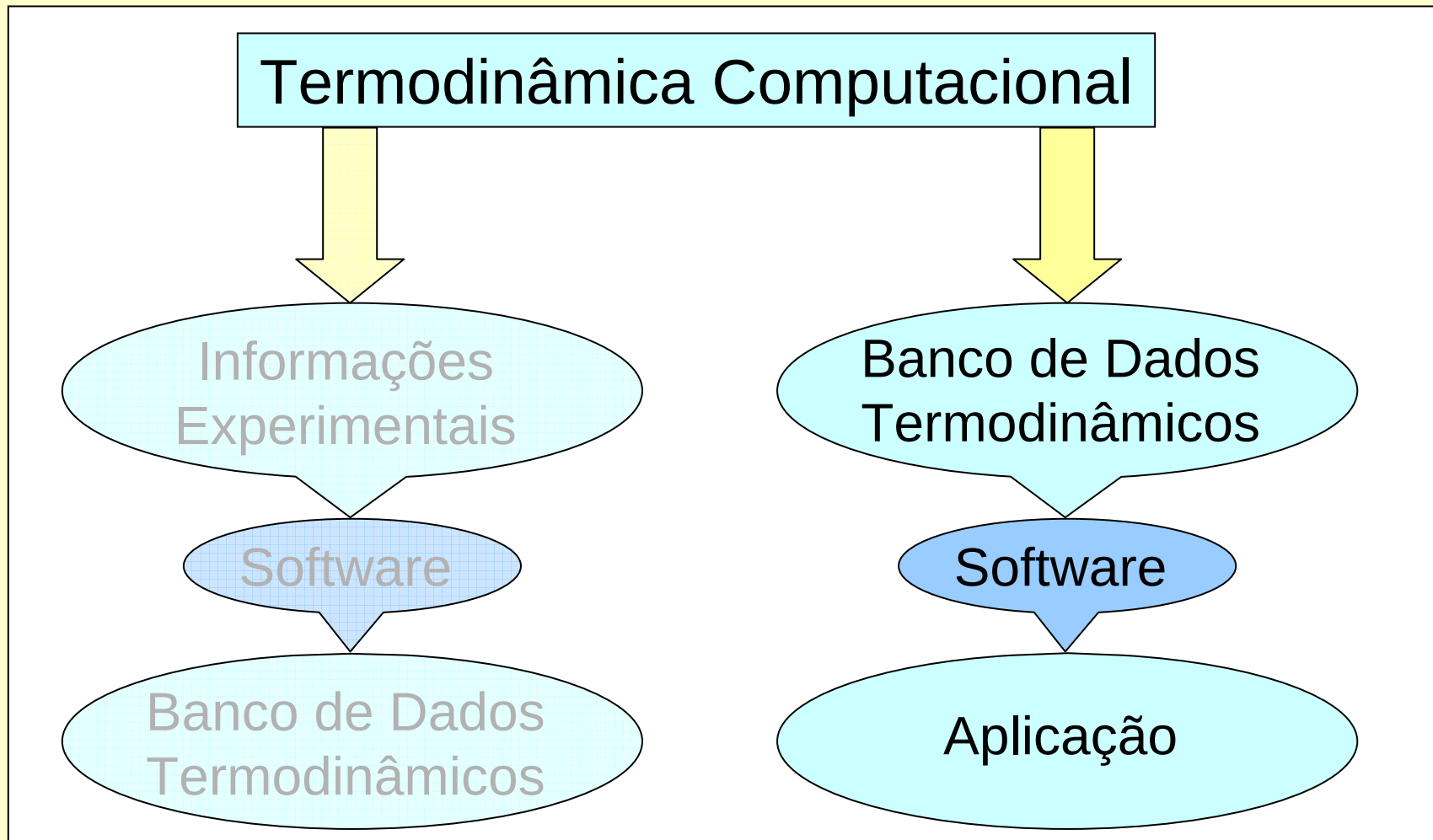
Termodinâmica Computacional

CALPHAD (CALculation of PHase Diagram)



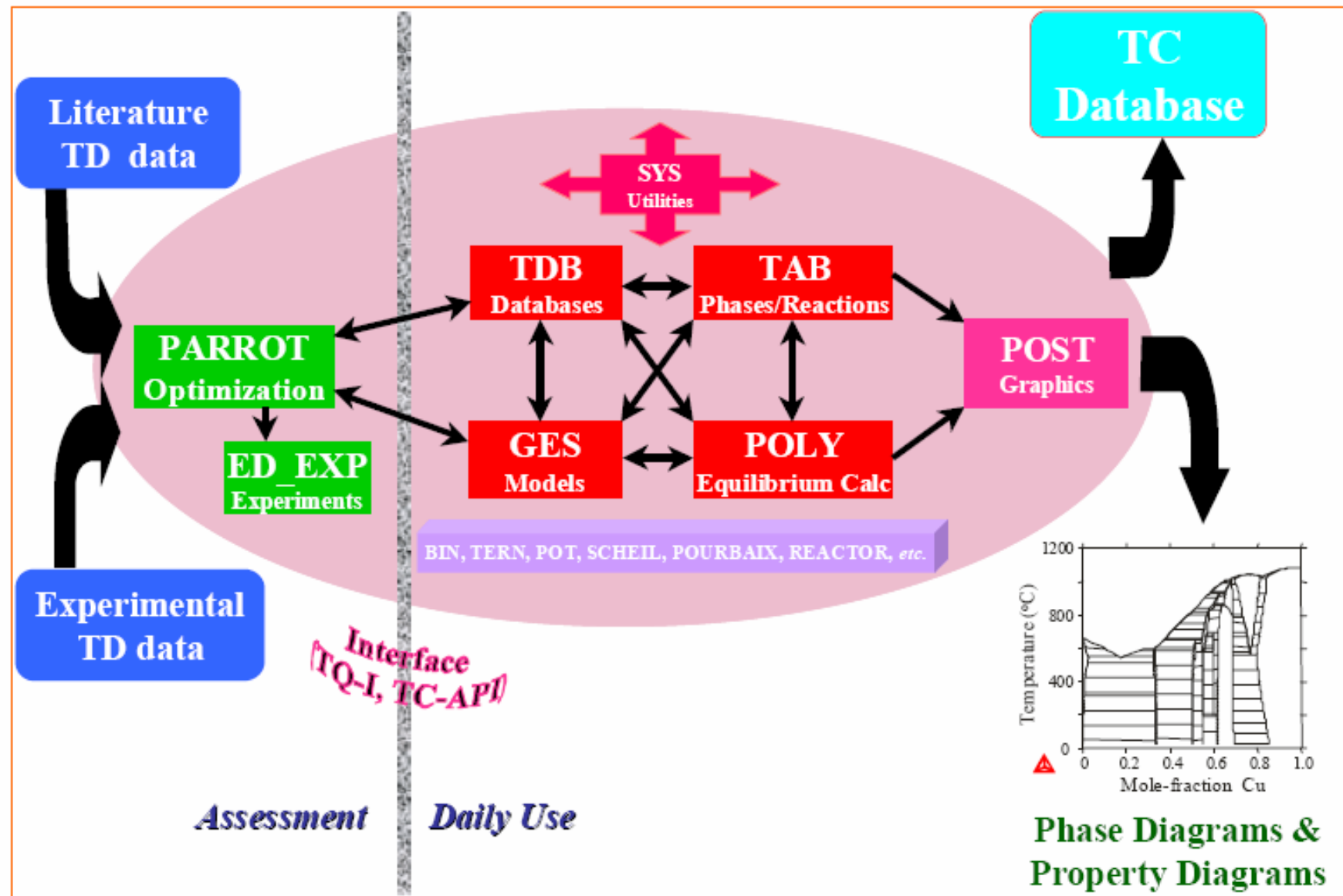
Termodinâmica Computacional

CALPHAD (CALculation of PHase Diagram)

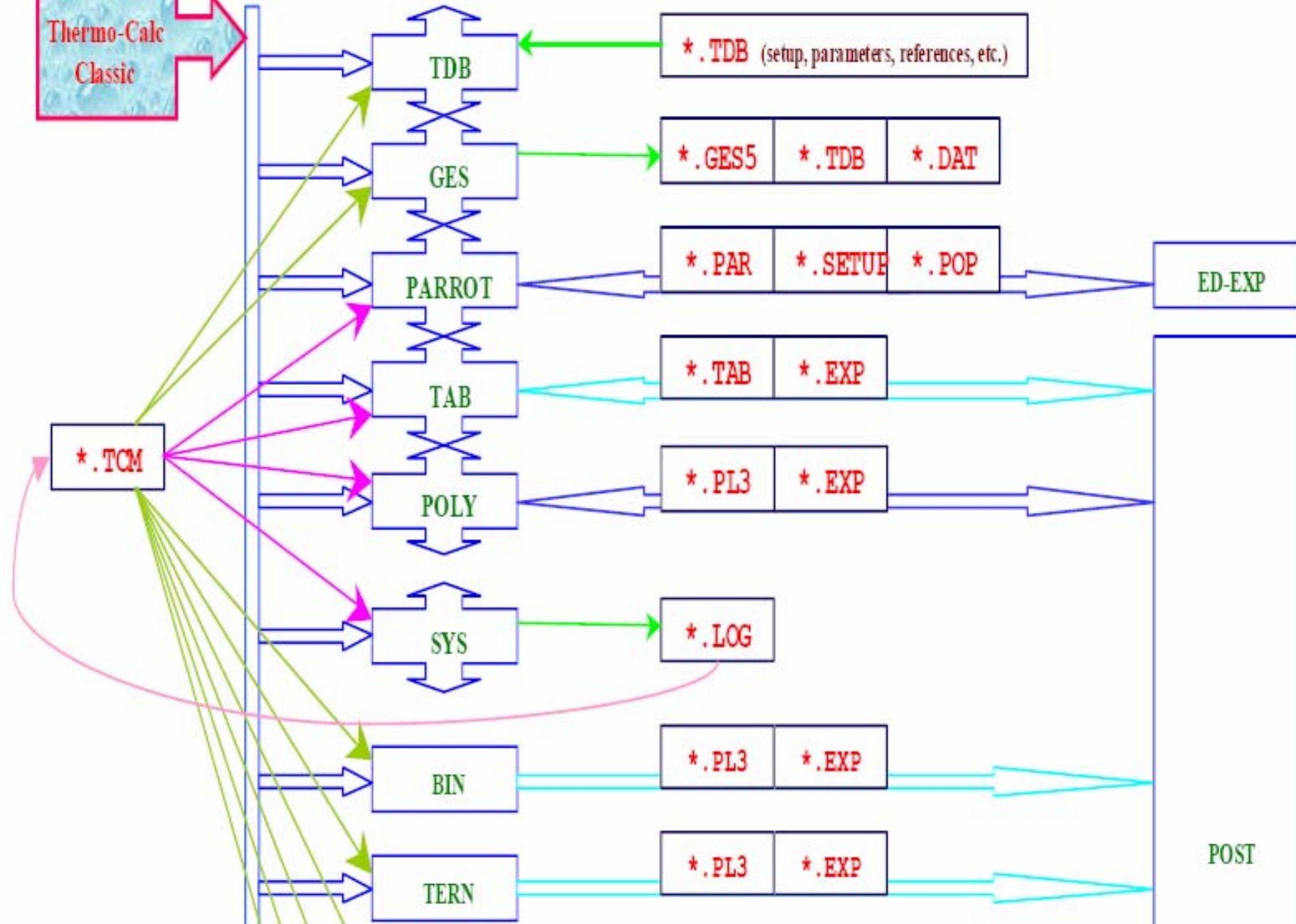


1.5 General Structure of the Thermo-Calc Package

The general structure of the Thermo-Calc package is illustrated in *Figure 1-2*.



Thermo-Calc
Classic



TCC Calculation Flowchart

Go data (TDB)

Getting data

```
switch/append <database name>
define_system <element names>
get_data
```

Go POLY

Calculate an equilibrium

```
set_condition to make the degree of
  freedom as zero
computer_equilibrium
list_equilibrium
```

Calculate a diagram

```
set_axis_variable to one condition
  you want to vary
save the status and conditions on POLY
  a file
step normal if you want to know how
  some properties vary with this
  condition (I.e., a property diagram)
set_axis_variable to another
  condition if you want to phase
  diagram, i.e., a diagram with zero
  phase fraction lines
map the lines with zero phase fractions.
```

Post

Plot a diagram

```
set_diagram_axis to the qualities
  you want to plot
set_plot_format to the graphical
  device you use
set_label_curve to the option you
  wish to identify the curves
plot the diagram. You may plot several
  diagrams with different types of axes
```

The following commands are available in the SYS module:

SYS:?

BACK	HP_CALCULATOR	SET_INTERACTIVE_MODE
CLOSE_FILE	INFORMATION	SET_LOG_FILE
EXIT	MACRO_FILE_OPEN	SET_PLOT_ENVIRONMENT
GOTO_MODULE	OPEN_FILE	SET_TERMINAL
HELP	SET_COMMAND_UNITS	STOP_ON_ERROR

SYS:

The following commands are available in the TDB module:

TDB_SSOL:?

AMEND_SELECTION	EXIT	NEW_DIRECTORY_FILE
APPEND_DATABASE	GET_DATA	REJECT
BACK	GOTO_MODULE	RESTORE
DATABASE_INFORMATION	HELP	SET_AUTO_APPEND_DATABASE
DEFINE_ELEMENTS	INFORMATION	SWITCH_DATABASE
DEFINE_SPECIES	LIST_DATABASE	
DEFINE_SYSTEM	LIST_SYSTEM	

TDB_SSOL:

The following commands are available in the POLY module:

POLY_3:?

ADD_INITIAL_EQUILIBRIUM	HELP	SELECT_EQUILIBRIUM
AMEND_STORED_EQUILIBRIA	INFORMATION	SET_ALL_START_VALUES
BACK	LIST_AXIS_VARIABLE	SET_AXIS_VARIABLE
CHANGE_STATUS	LIST_CONDITIONS	SET_CONDITION
COMPUTE_EQUILIBRIUM	LIST_EQUILIBRIUM	SET_INPUT_AMOUNTS
COMPUTE_TRANSITION	LIST_INITIAL_EQUILIBRIA	SET_INTERACTIVE
CREATE_NEW_EQUILIBRIUM	LIST_STATUS	SET_MINIMIZATION_OPTIONS
DEFINE_COMPONENTS	LIST_SYMBOLS	SET_NUMERICAL_LIMITS
DEFINE_DIAGRAM	LOAD_INITIAL_EQUILIBRIUM	SET_REFERENCE_STATE
DEFINE_MATERIAL	MACRO_FILE_OPEN	SET_START_CONSTITUTION
DELETE_INITIAL_EQUILIB	MAP	SET_START_VALUE
DELETE_SYMBOL	POST	SHOW_VALUE
ENTER_SYMBOL	READ_WORKSPACES	SPECIAL_OPTIONS
EVALUATE_FUNCTIONS	RECOVER_START_VALUES	STEP_WITH_OPTIONS
EXIT	REINITIATE_MODULE	TABULATE
GOTO_MODULE	SAVE_WORKSPACES	

POLY_3:

The following commands are available in the POST module:

POST:?

ADD_LABEL_TEXT	PLOT_DIAGRAM	SET_LABEL_CURVE_OPTION
APPEND_EXPERIMENTAL_DATA	PRINT_DIAGRAM	SET_PLOT_FORMAT
BACK	QUICK_EXPERIMENTAL_PLOT	SET_PLOT_OPTIONS
CREATE_3D_PLOTFILE	REINITIATE_PLOT_SETTINGS	SET_PLOT_SIZE
DUMP_DIAGRAM	RESTORE_PHASE_IN_PLOT	SET_PREFIX_SCALING
ENTER_SYMBOL	SET_AXIS_LENGTH	SET_RASTER_STATUS
EXIT	SET_AXIS_PLOT_STATUS	SET_REFERENCE_STATE
FIND_LINE	SET_AXIS_TEXT_STATUS	SET_SCALING_STATUS
HELP	SET_AXIS_TYPE	SET_TIC_TYPE
LIST_DATA_TABLE	SET_COLOR	SET_TIELINE_STATUS
LIST_PLOT_SETTINGS	SET_CORNER_TEXT	SET_TITLE
LIST_SYMBOLS	SET_DIAGRAM_AXIS	SET_TRUE_MANUAL_SCALING
MAKE_EXPERIMENTAL_DATAFI	SET_DIAGRAM_TYPE	SUSPEND_PHASE_IN_PLOT
MODIFY_LABEL_TEXT	SET_FONT	TABULATE
PATCH_WORKSPACE	SET_INTERACTIVE_MODE	

POST:

Note that the DUMP_DIAGRAM and PRINT_DIAGRAM commands are only valid under PC Windows environments.