ThermoFAST

Thermodynamic Calculation Tool

User Manual

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FLUID SCIENCE & RESOURCES

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1 Introduction

ThermoFAST is a thermodynamic property calculator for LNG and natural gas with the ability to perform vapour-liquid-solid equilibrium calculations, predict conditions at which solid formation can occur in complex, multi-component systems and generate full phase envelopes.

If more information regarding the thermodynamic models or algorithms used in ThermoFAST, please refer to the following Doctoral Thesis.

Baker, CJ 2018, *Phase equilibrium measurements and advanced modelling for optimising liquefied natural gas production*, Doctor of Philosophy, The University of Western Australia. https://doi.org/10.26182/5bc411e7ccc0d

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4 Installation Folders

All the following files and folders must be stored in the same directory in order to utilise them internally; however only the "ESSENTIAL" components are required to run ThermoFAST.

Name	Type	Description
ThermoFAST.exe	ESSENTIAL	Primary executable
TREND.dll	NOT ESSENTIAL	Provides access to the reference equation of state GERG-2008 and improved Combustion Gas equations powered by TREND*
ThermoFAST [Folder]	NOT ESSENTIAL	Folder that provides ThermoFAST with quick access to the following sub-folders **1.** Saved Files **2.** Custom Binary Interaction Parameters **3.** Custom Component Properties **4.** Custom Fluid Files **5.** Documents

* Span, R.; Eckermann, T.; Herrig, S.; Hielscher, S.; Jäger, A.; Thol, M. (2016): TREND. Thermodynamic Reference and Engineering Data 3.0. Lehrstuhl für Thermodynamik, Ruhr-Universität Bochum.

5 Menu Items

5.1 File

Name	Description
Save	Saves the current configuration using the previous save or load file name and location including units, component properties, models, composition, flash and solid calculations including solid diagrams. It is recommended to save to the recommended file location for quick and efficient access. If no previous saves or loads have been performed on the current instance of ThermoFAST then the *Save As* function will be utilised.
Save As	Save a new case folder to the recommended or a custom directory
Load	Loads a previously saved case folder. The *Load* function loads a saved folder of .txt files and therefore it is necessary to open the desired *Load* folder and then simply click open again once the .txt files appear. This will

Name	Description
	load all the required files in the selected case folder. It is not necessary to select any of the individual .txt files.
Reset	Resets the window to the default settings (deleting all selected components and calculation results)
Exit	Exits ThermoFAST, closing all associated windows

TIP # 1: Saving to the recommended file location will cause previous cases to appear in the drop down menu located in the "Load" function for quick access

5.2 Models

Name	Description
Equation of State	Selected equation of state, where the recommended package tuned for solid predictions is Peng-Robinson (1976).
Mixing Rules + Interaction Parameters	Selected type of mixing rule in the drop-down box. The button 'View' button loads multiple data sets containing binary interaction parameters (BIPs) available for user selection. In some versions of ThermoFAST the user is able to edit the BIPs and save a data set for future quick access.
Solid Equilibrium	Type of approach taken for solid equilibrium calculations. The default approach utilises the cubic equation of state to calculate the fugacity of the solvent. Other methods (not available in ThermoFAST) use activity coefficient models.
Solid Density	Selected model for density of a pure solid
Hydrates	Selected hydrate model. Only available in specific versions of ThermoFAST; please contact the developers or visit their website for information on how to obtain this version. TREND has an inbuilt hydrate model that utilises the Helmholtz equation in the Improved Combustion Gas version only

TIP # 2: If a custom binary interaction parameter data set is saved by the user it will appear in the **ThermoFAST/Custom Binary Interaction Parameters** folder in the same directory as ThermoFAST.exe

5.3 Help

Name	Description
User Manual	Obtain a copy of this user-manual through the user interface
About Us	Description of ThermoFAST and acknowledgements
Contact Developers	Contact the developers for future updates and troubleshooting
How to Cite us	Shows the citation for the current version of ThermoFAST
Disclaimer	ThermoFAST's official disclaimer regarding the appropriate use of this product

TIP # 3: A copy of the user manual will be saved in the **ThermoFAST/Documents** folder in the same directory as ThermoFAST.exe

6 User Interface

6.1 Units

Name	Description
SI (K, MPa, mol, J)	Custom set of International System inspired units tailored to academic and research areas (metric)
SI (°C, bar, kg, J)	Custom set of International System inspired units tailored to plant and operational data (metric)
Field (°F, psia, lbmol, BTU)	Custom set of Field (Imperial) units
Custom	Allows the user to select a combination of units based on preference; composition, temperature, pressure, density, heat capacity and enthalpy. Heat capacity and Heat of Fusion (units of enthalpy) are required in the calculation of solid equilibrium.

6.2 FLUID

Name	Description
Fluid	Choose a saved fluid (if applicable), otherwise a custom mixture is automatically created
Available	Global list of available components
Selected	Components that have been selected for calculations
< Move Selected >	Selected components will be moved to the opposite list

Name	Description
CLEAR ALL	Remove all “Selected” components. Note this will reset various outputs associated with this mixture.
EDIT COMPONENT PROPRERTIES	View or edit the selected component properties depending on the version of ThermoFAST. Save functionality is available in the editable version allowing users to save custom sets to the “Custom Component Properties” folder. If a name already exists it will overwrite that data set.
Allow Ice to Form	This checkbox appears when a mixture containing water is selected. The formation of ice from trace concentrations of water in LNG mixtures at cryogenic temperatures is difficult to measure and not well understood. Standard industry specifications for the maximum allowable water content in LNG to avoid ice formation are in the range 0.1 to 1 ppm. However, at these trace concentrations most thermodynamic models capable of predicting solid ice formation indicate ice should be stable at temperatures as high as 200 K. If the user is interested in the formation of other cryogenic solids then it is advisable to leave this box unchecked. This option only applies to the 'FLASH' and 'SOLIDS' calculators.

TIP # 4: Multiple components can be selected by holding down control and/or shift

TIP # 5: Double clicking a component moves it to the opposite list

TIP # 6: If a component property data set is saved by the user it will appear in the **ThermoFAST/Custom Component Properties** folder in the same directory as ThermoFAST.exe

6.3 COMPOSITION

Name	Description
Fluid	Choose a saved fluid (if applicable), otherwise a custom mixture is automatically created

Name	Description
Basis	Select the composition basis: mass or molar
Save Fluid	Saves a custom defined fluid and a range of compositions. The fluid is saved in a location that allows ThermoFAST quick access.
Delete Saved Fluid	Deletes the fluid that is currently selected. If the "custom mixture" is selected it will simply wipe all data.
Allow Ice and Hydrates to Form	This checkbox appears when a mixture containing water is selected. The formation of ice from trace concentrations of water in LNG mixtures at cryogenic temperatures is difficult to measure and not well understood. Standard industry specifications for the maximum allowable water content in LNG to avoid ice formation are in the range 0.1 to 1 ppm. However, at these trace concentrations most thermodynamic models capable of predicting solid ice formation indicate ice should be stable at temperatures as high as 200 K. If the user is interested in the formation of other cryogenic solids then it is advisable to leave this box unchecked. This option only applies to the 'FLASH' and 'SOLIDS' calculators.
VIEW PHASE ENVELOPE	Calculates the phase envelope of the mixture in the adjacent option box in the case of multiple compositions.
NORMALISE	Normalise all compositions - this is not essential but can be helpful
CLEAR ALL	Clears all compositions but does not clear selected components
COPY DATA	Copy all compositions and component names to the clipboard for easy integration into Excel
Normalised Status	Checks whether all compositions sum to 1 or zero

TIP # 7: Multiple mixtures can be considered by simply entering in a new composition in each subsequent column.

TIP # 8: Calculations will run with un-normalised compositions (they are normalised internally).

TIP # 9: Users can select what data to copy to the clipboard by simply right clicking any selected data and pressing "copy" or using the shortcut "control" + "c". Then simply right click in Excel and click "paste" to output the data, or use the shortcut "control" + "v".

TIP # 10: If a custom fluid and a range of compositions is saved by the user it will appear in the **ThermoFAST/Custom Fluid Files** folder, located in the same directory as ThermoFAST.exe

6.4 FLASH

Name	Description
CONDITIONS	Performs flash calculations at a specified temperature and pressure to output the phase fractions and properties
COMPONENTS	Outputs the compositions of the component phases
Component Amounts	Select the component unit basis: mass or molar basis
Mixture Number	Corresponds to the mixture number under the "COMPOSITION" tab
LOCATE	**Temperature-Pressure Flash**: perform a T-P flash **Bubble Point Temperature**: locates the bubble point temperature at a given pressure and composition **Bubble Point Pressure**: locates the bubble point pressure at a given temperature and composition **Dew Point Temperature**: locates the dew point temperature at a given pressure and composition **Dew Point Pressure**: locates the dew point pressure at a given temperature and composition
Locate _____ **(Checkbox that appears)**	Appears when a bubble or dew point calculation is selected. In some systems there may be two conditions at which a dew or bubble point exists at the specified temperature or pressure. Selecting this checkbox will force the algorithm to return the condition that satisfies the nominated constraint; if it is unchecked, the returned condition will be the other possibility if one exists.
CALCULATE	Performs the desired calculation
CLEAR ALL	Deletes all inputs and outputs
COPY DATA	Copy all inputs and outputs to the clipboard for easy integration into Excel

TIP # 11: Although the mixture number is unique to each composition, if more flash conditions exist than there are mixture numbers, it will simply perform a flash calculation on the composition associated with the most recent mixture number. Therefore, there is no need to re-enter the same composition to perform multiple flash calculations of the same mixture.

TIP # 12: If more than one solid component exists then a combined solid density will be shown; however this is only used as an indicator. Unlike vapour and liquid phases, solids are not homogenous mixtures and each solid compound is treated as a separate solid phase (for this reason the "COMPONENTS" tab reports solid fractions, rather than the solid composition). The density of the individual solid can be found by simply choosing the pure component and specifying the same temperature and pressure.

6.5 SOLIDS

ThermoFAST is able to locate solid transition region temperatures or maximum solid concentrations for the selected mixture number. It has the ability to locate different types of solid phase equilibrium; solid-vapour, solid-vapour-liquid and solid-liquid equilibrium (solid-solid can be found under a normal "FLASH" calculation). The algorithm searches at constant pressure for the highest temperature at which a solid phase appears; thereafter it searches for and reports subsequent phase transitions that occur at lower temperatures. A detailed description of all possible transitions that can be located is provided in section 6.5.3 with illustrations.

6.5.1 SEARCH

Name	Description
TEMPERATURE	Used to specify and report the search results for the temperatures at which solid phase transitions occur for a given mixture at a specified temperature. The user must specify the pressure at which to search ("Input Pressure"). Multiple pressures or multiple mixture numbers can be specified. **Locate Melting Temperature at Bubble Point Pressure:** If checked, ThermoFAST will search for the triple point condition where the bubble point meets the melting point. Solid equilibrium experiments are often conducted along the liquid's bubble point curve and in many

Name	Description
	cases the system pressure is not reported. For this search the composition of the liquid phase (rather than the overall composition) must be specified. Computation can be slow and this triple point may not exist in all systems which will result in an unstable condition.
CONCENTRATION	Used to specify and report the search results for the maximum mole fraction of the solute that the solution can hold at the specified temperature and pressure. The user must specify the temperature and pressure ("Input Temperature" and "Input Pressure") at which to calculate the solute concentration. The user can also specify a different solute to that recommended using the drop down menu. Multiple pressures or multiple mixture numbers can be specified. In cases where the algorithm is becomes unstable a range of melting temperatures or concentrations at the specified pressure. The user also has the option of additionally viewing all temperatures at which a phase transition occurs at the given pressure and calculated composition.
CALCULATE	Executes the search algorithm selected via either "**TEMPERATURE**" or "**CONCENTRATION"** above.
CLEAR ALL	Deletes all search inputs and outputs for the solids search
COPY DATA	Copy all solid search inputs and outputs to the clipboard in a format easily pasted into Excel.
DICTIONARY OF PHASE TRANSITIONS	Provides descriptions of the phase transitions that may be returned by the solids search algorithm, similar to those provided in section 6.5.3

6.5.2 GRAPH

Name	Description
GRAPH	Allows the user to calculate solubility curves, solid phase diagrams and a eutectic diagram (temperature-composition plot) for a selected mixture

Name	Description
Selected Mixture	Performs the calculations with the mixture number corresponding to the "COMPOSITION" tab
SOLUBILITY	Calculates a solubility curve for the selected mixture at a constant pressure. The user is able to choose the solute that will solidify. Solidification of other components in the mixture will then not be considered by the calculation. The user selects concentration unit type and a range of concentration over which to calculate the corresponding melting temperature. For binary systems it is not necessary to specify the mixture composition because the solvent is sufficiently defined.
SOLID PHASE	Calculates a pressure-temperature diagram for a given mixture at which the solid phase transitions are indicated. The mixture composition must be defined. Essentially the Solid Search function is executed at the number of pressures specified by the user within the selected pressure range.
EUTECTIC	Calculates a graph containing the different solid transition regions versus the selected component's composition. This will also locate the eutectic point where composition of the selected component produces the mixture's lowest melting temperature (Eutectic Temperature). This search also locates triple points.
CALCULATE _____	Calculates the selected graph if sufficient information is has been provided by the user.
SHOW GRAPH	This button will appear upon completion of the graphing calculation, allowing the user to view the results.

TIP # 13: The user is able to copy the graph's outputs to the clipboard for easy integration to Excel once the "SHOW GRAPH" button is pushed

6.5.3 TYPES OF TRANSITION POINTS

Table 6.1 presents the Baker-May classification of transition pathways related to solid-fluid equilibrium that were identified using ThermoFAST. The classification also indicates whether

each transition pathway can be the highest solid-fluid equilibrium temperature (HSET) and/or occur at a temperature below the HSET. Some of these transition pathways are only possible in multi-component mixtures as a consequence of Gibbs Phase rule. Correctly identifying which type of transition is associated with the appearance of a solid phase at a given condition is important in an LNG production context because processing in upstream operations can in principle produce a fluid mixture containing no solids that is initially at a condition below its HSET. Please refer to the following Doctoral Thesis for further detail on the Baker-May classification table:

Baker, CJ 2018, *Phase equilibrium measurements and advanced modelling for optimising liquefied natural gas production*, Doctor of Philosophy, The University of Western Australia. https://doi.org/10.26182/5bc411e7ccc0d

Table 6.1: The Baker-May classification of transition pathways involving solid-fluid equilibrium for pure fluids and mixtures. The ability for the transition to be the highest solid-fluid equilibrium temperature (HSET) and/or occur at a temperature below HSET is also indicated.

Path	*Can be HSET?*	*Can be below HSET?*	*Description of Transition*
			Pure Fluids Only[#]
#1	True	False	Liquid to Solid*
#2	True	False	Vapour to Solid*
			Multicomponent Mixtures (≥ 2 components)
#3	True	False	Vapour to SVE
#4	True	False	VLE to SVE
#5	True	True	Liquid to SLE
#6	True	False	Liquid to SLE (Liquid Retrograde)
#7	False	True	SLE (Liquid Retrograde) to SVE (SLVE)
#8	False	True	SVE to SLE (SLVE)
#9	False	True	SVE to SLE (Solid Retrograde)
#10	False	True	SLE (Solid Retrograde) to SLE (Normal)^
#11	False	True	SVE to SVE (Solid Retrograde)^
#12	False	True	SVE to VLE (SLVE) [or SVE (Solid Retrograde) to VLE]
#13	False	True	VLE to Liquid
#14	False	True	SLE (Solid Retrograde) to Liquid
#15	False	True	SVE to Liquid [or SVE (Solid Retrograde) to Liquid]
			Multicomponent Mixtures (≥ 3 components)
#16	True	False	VLE to SLVE (Liquid Retrograde)
#17	True	False	VLE to SLVE
#18	False	True	SLE (Liquid Retrograde) to SLVE
#19	False	True	SLE (Liquid Retrograde) to SLVE (Liquid Retrograde)
#20	False	True	SLVE (Liquid Retrograde) to SVE
#21	False	True	SLVE to SLE (Solid Retrograde)
#22	False	True	SLVE to SLE
#23	False	True	SVE to SLVE
#24	False	True	SVE to SLVE (Solid Retrograde)
#25	False	True	SLVE (Solid Retrograde) to Liquid
#26	False	True	SLVE (Solid Retrograde) to VLE

Binary mixtures at their Eutectic compositions can also undergo these transitions

* the special case of a pathway that passes through the pure fluid's triple point is considered an intersecting subset of pathway #1 and #2

^ Pathways are not phase transitions since no new phase appears. They are termed "retrograde-only transitions" as they correspond to the location of either a minimum or a maximum in the amount of solid phase with decreasing temperature

6.6 TUNE

The user has a powerful tool for tuning the binary interaction parameters for specific component sets using the selected equation of state. The user can tune to solid formation and bubble point conditions, as well as vapour-liquid compositions. The user will then be able to manually add these tuned binary interaction parameters to custom data sets under the *Models* menu item.

Name	Description
BINARIES	Select the components to tune and set the starting binary interaction parameters based on the selected mixing rule. A good initial estimate may be required, this is common practice when using a muli-parameter mixing rules. It is recommended to use a higher starting value for solid data ($0.01 < k_{ij} < 0.1$ and $C_{ij} = 1$).
CRITERIA	Select from a variety of data types to tune from including solid formation, bubble point conditions and vapour-liquid compositions. Select the type of objective function (absolute or relative), absolute is recommended for vapour-liquid composition data. Select the tolerance of the binary interaction parameter(s) and the maximum number of iterations before stopping the calculation.
DATA	Input the data that ThermoFAST will use to tune the binary interaction parameter(s). The sub-categories represent the objective functions selected under *CRITERIA*. In regards to *SOLID* data, the user may also tune to the triple point for solid calculations (the boundary at which the bubble point meets the melting point and therefore a pressure is not required).
CLEAR ALL	Deletes all inputs and outputs (resets the tuning interface)
COPY DATA	Copy the tables under *DATA* or *OUTPUTS* to the clipboard for easy integration into Excel

Name	Description
OUTPUTS	View the tuning results. The user can view the optimised binary interaction parameter and results as the tuning is progressing (before the completion criteria is met).

TIP # 14: If the tuning calculation has ended, the user can simply click TUNE DATA again to begin tuning to the most recently optimised binary interaction parameter and these are updated under the BINARIES tab.