

Getting started with Simulis® Thermodynamics

Use Case 6: Defining the decomposition of pure components in order to use group contribution models

Software & Services In Process Simulation

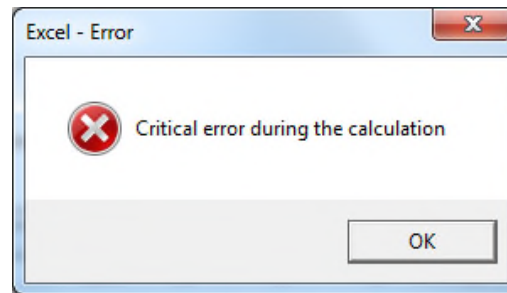
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ProSim

Introduction

The following message may appear when you are using a predictive thermodynamic model such as UNIFAC or PPR78:



In most of the cases, this message corresponds to missing information about the mixture, in particular concerning the decomposition of the mixture components.

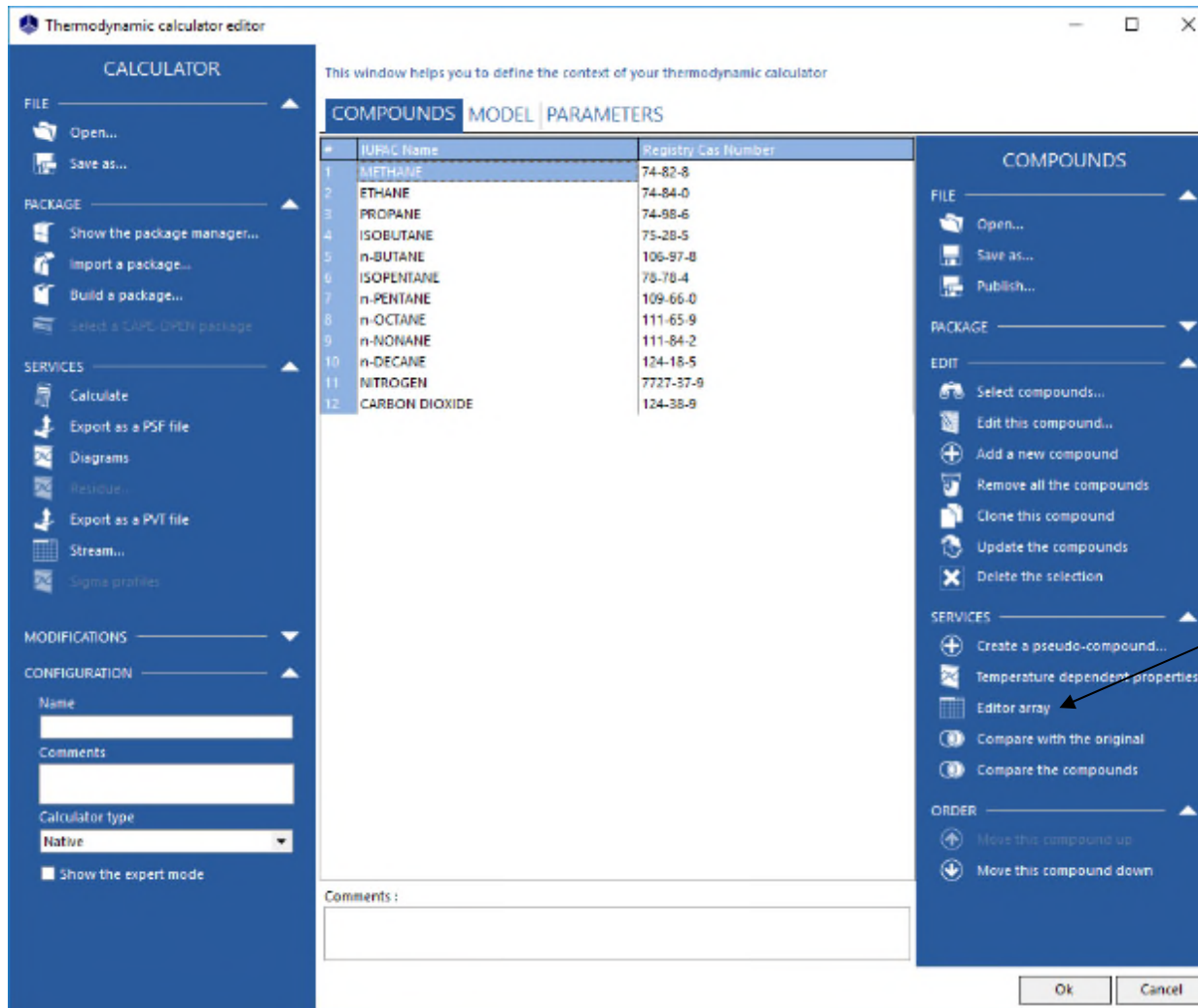
The following steps show how to add the required decomposition information.

In this example, the mixture contains the following components: methane, ethane, propane, isobutane, n-butane, isopentane, n-pentane, n-heptane, n-octane, n-nonane, n-decane, nitrogen and carbon dioxide.

The Unifac VTPR thermodynamic model is selected.

At this stage, it is assumed that components and thermodynamic models were already selected. For more information on this step, please consult "*Getting started with Simulis Thermodynamics, Case 1*".

Step 1: Edit the calculator



Open the
**Thermodynamic
calculator editor** and
click on **“Editor array”**.

Step 1: Edit the calculator

Compound Editor

COMPOUNDS

PROPERTIES

VIEW

MODIFICATIONS

UNIT SYSTEMS

This window helps you visualize the compounds properties.

Complete

Properties	METHANE	ETHANE	PROPANE	ISOBUTANE	n-BUTANE	ISOPENTANE	n-PENTANE	n-OCTANE	n-NONANE	n-DECANE	NITROGEN	CARBON DIOXIDE
Identification												
Group contribution m...												
Standard												
UNIFAC modifie... [CH4] 1	[CH3] 2	[CH3] 2	[CH3] 2 [CH2] 1	[CH3] 3 [CH] 1	[CH3] 2 [CH2] 2	[CH3] 3 [CH2] 1 [...]	[CH3] 2 [CH2] 3	[CH3] 2 [CH2] 6	[CH3] 2 [CH2] 7	[CH3] 2 [CH2] 8	[NITROGEN] 1	[CARBON D] 1
UNIFAC origina... <unknown>	[CH3] 2	[CH3] 2	[CH3] 2 [CH2] 1	[CH3] 3 [CH] 1	[CH3] 2 [CH2] 2	[CH3] 3 [CH2] 1 [...]	[CH3] 2 [CH2] 3	[CH3] 2 [CH2] 6	[CH3] 2 [CH2] 7	[CH3] 2 [CH2] 8	<unknown>	<unknown>
UNIFAC PSRK c... [CH4] 1	[CH3] 2	[CH3] 2	[CH3] 2 [CH2] 1	[CH3] 3 [CH] 1	[CH3] 2 [CH2] 2	[CH3] 3 [CH2] 1 [...]	[CH3] 2 [CH2] 3	[CH3] 2 [CH2] 6	[CH3] 2 [CH2] 7	[CH3] 2 [CH2] 8	[N2] 1	[CO2] 1
UNIFAC LLE che... <unknown>	[CH3] 2	[CH3] 2	[CH3] 2 [CH2] 1	[CH3] 3 [CH] 1	[CH3] 2 [CH2] 2	[CH3] 3 [CH2] 1 [...]	[CH3] 2 [CH2] 3	[CH3] 2 [CH2] 6	[CH3] 2 [CH2] 7	[CH3] 2 [CH2] 8	<unknown>	<unknown>
UNIFAC modifie... <unknown>	[CH3] 2	[CH3] 2	[CH3] 2 [CH2] 1	[CH3] 3 [CH] 1	[CH3] 2 [CH2] 2	[CH3] 3 [CH2] 1 [...]	[CH3] 2 [CH2] 3	[CH3] 2 [CH2] 6	[CH3] 2 [CH2] 7	[CH3] 2 [CH2] 8	<unknown>	<unknown>
UNIFAC modifie... [CH4] 1	[C2H6] 1	[C3H8] 1	[C4H10] 1	[C4H10] 1	[C4H10] 1	[CH3] 3 [CH2] 1 [...]	[CH3] 2 [CH2] 3	[CH3] 2 [CH2] 6	[CH3] 2 [CH2] 7	[CH3] 2 [CH2] 8	[N2] 1	[CO2] 1
PPR 78 chemical... [CH4] 1	[C2H6] 1	[CH3] 2 [CH2] 1	[CH3] 3 [CH] 1	[CH3] 2 [CH2] 2	[CH3] 3 [CH2] 1 [...]	[CH3] 2 [CH2] 3	[CH3] 2 [CH2] 6	[CH3] 2 [CH2] 7	[CH3] 2 [CH2] 8	[CH3] 2 [CH2] 8	[N2] 1	[CO2] 1
UNIFAC VTPR c...	<unknown>	<unknown>	<unknown>	<unknown>	<unknown>	<unknown>	<unknown>	<unknown>	<unknown>	<unknown>	<unknown>	<unknown>
UNIFAC UMRPP...	<unknown>	<unknown>	<unknown>	<unknown>	<unknown>	<unknown>	<unknown>	<unknown>	<unknown>	<unknown>	<unknown>	<unknown>
NRTL PR chemi... [CH4] 1	[C2H6] 1	[CH3] 2 [CH2] 1	[CH3] 3 [CH] 1	[CH3] 2 [CH2] 2	[CH3] 3 [CH2] 1 [...]	[CH3] 2 [CH2] 3	[CH3] 2 [CH2] 6	[CH3] 2 [CH2] 7	[CH3] 2 [CH2] 8	[CH3] 2 [CH2] 8	[N2] 1	[CO2] 1
GC-PPC-SAFT ch... [METHANE] (0, 0) 1	[ETHANE] (0, 0) 1	[CH3] (1, 0) 2 [CH2]...	[CH3] (2, 0) 3 [CH] (...]	[CH3] (1, 0) 2 [CH2]...	[CH3] (2, 0) 2 [CH] (...]	[CH3] (1, 0) 2 [CH2]...	[CH3] (1, 0) 2 [CH2]...	[CH3] (1, 0) 2 [CH2]...	[CH3] (1, 0) 2 [CH2]...	[CH3] (1, 0) 2 [CH2]...	[NITROGEN] (0, 0) 1	<unknown>
User												
Atomic												
Phase change												
Combustion, security, t...												
Condensed phase												
Phase thermochemistry												
Interaction, gas phase ...												
User properties												
PPC-SAFT												
NRTL-SAC												
Temperature depende...												

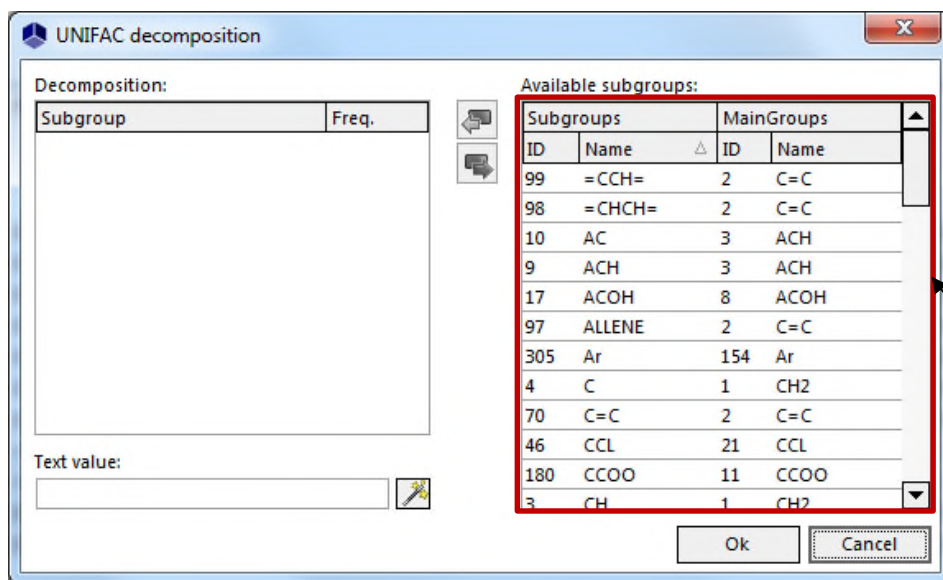
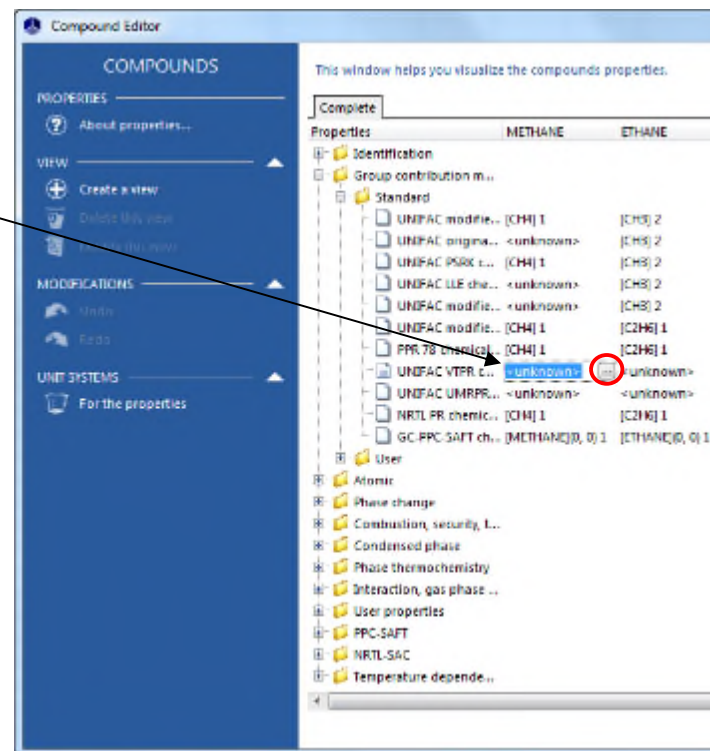
Ok Cancel

The decompositions that are available for the different thermodynamic models are displayed in the “Group contribution model” tab.

We can see that the decompositions are missing (marked as “unknown”) for the UNIFAC VTPR model.

Step 2: fill out the missing information

Click on the "*unknown*" field, then click on the 3 dots that appear.



The decomposition window opens.

The available subgroups for this specific thermodynamic model are presented on the right side of the window.

Step 2: fill out the missing information

There are 2 different methods to obtain the group decomposition of a compound:

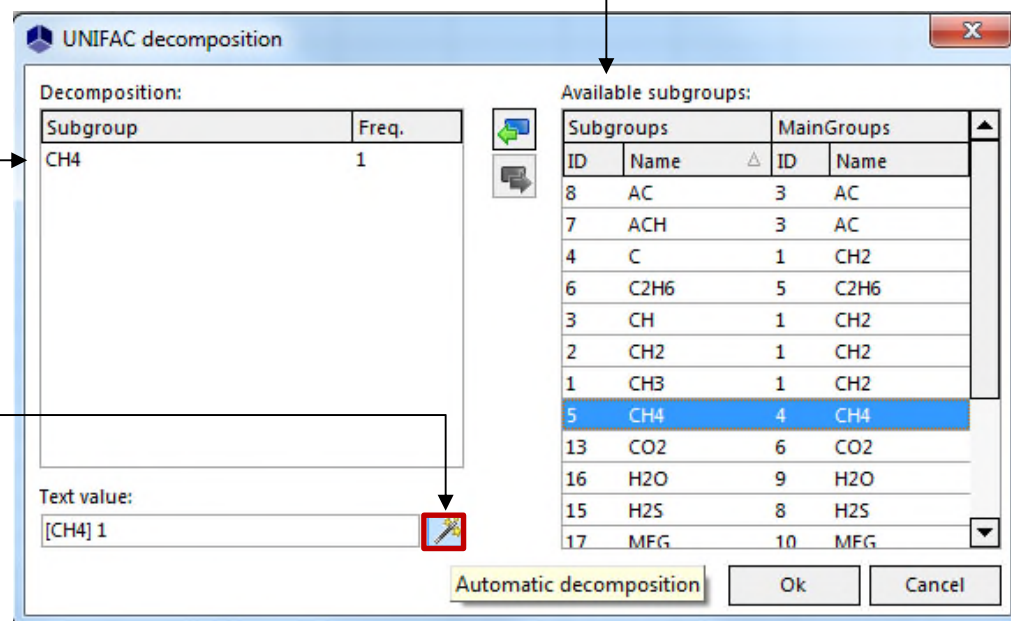
Manual method:

Double-click on the subgroups corresponding to the chemical structure of the component.

The subgroups that are selected, along with their frequency in the molecule, are displayed on the left part of the window.

Automatic method:

Click on the wand icon. The group decomposition will be automatically generated from the SMILES.

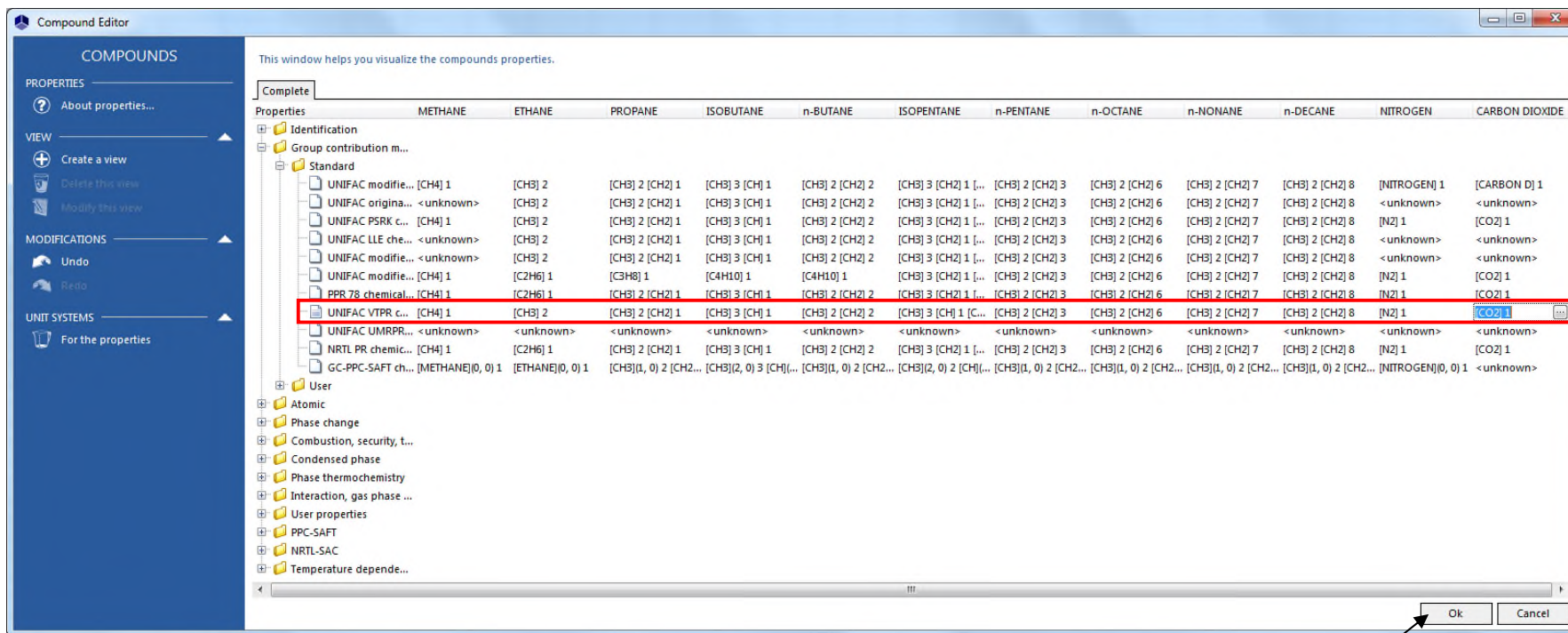


The automatic method can be used if the SMILES of the compound has been provided and if the corresponding subgroups are available for the selected thermodynamic model.

Step 3: complete the operation and confirm

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Repeat the operation until all the fields are defined for the selected model.



In order to use a group contribution model, the decomposition of all the compounds must be provided for this specific model.

Click on "OK" to confirm. You can now use UNIFAC VTPR thermodynamic model for this mixture.

Step 3: complete the operation and confirm

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When a predictive model is selected in the “*Model*” tab, it is possible to access the parameters of the groups (and subgroups) corresponding to the compounds imported in the calculator.

Thermodynamic calculator editor

FILE — Open... Save as... PACKAGE — SERVICES — Calculate Export as a PSF file Diagrams Residue... Export as a PVT file Stream... Sigma profiles MODIFICATIONS — CONFIGURATION —

NAME: H₂O-LiBr
Comments:
Calculator type: Native
☐ Show the expert mode

COMPOUNDS MODEL PARAMETERS

This window helps you to define the context of your thermodynamic calculator

Name: VTPR
Category: All the profiles
Profile: VTPR

Approach type: Using Equation of state
Equation of state: PR Generalized
Alpha function: Twu
Mixing rules: VTPR
Activity coefficient model: UNIFAC VTPR
Pure liquid fugacity standard state: Standard
Liquid molar volume: Volume translation
Transport properties: Ely-Hanley model (TRAPP method)
Enthalpy calculation: H*=0, ideal gas, 25°C, 1 atm
User-defined thermodynamic model: None
Model index: 1

Comments:

THERMODYNAMIC MODEL

DOCUMENTATION — Thermodynamic assistant Thermodynamic help

ADDITIONAL PARAMETERS —

MODEL INFORMATION —

Reactive model parameters...
Predictive model parameters...
Polymers model parameters...

WATER-HYDROCARBON —
PURE WATER —

Ok Cancel

Click on “*Predictive model parameters*”.

Step 3: complete the operation and confirm

The following window appears, displaying the decomposition obtained for the selected predictive model:

Predictive models editor:

Zoom : 100 %

Legend:

- No parameter
- 1 parameter
- 2 parameters
- 3 parameters

Matrix visualization:

	1	151	152
1	CH2		
151	CO2		
152	CH4		
155	N2		

Table of parameters:

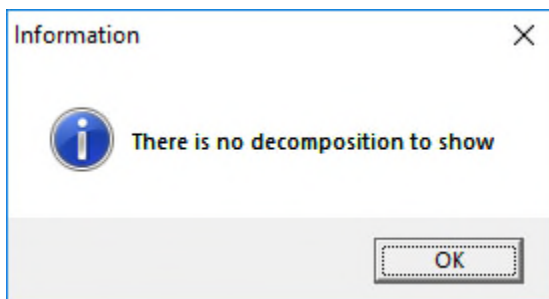
Main groups	Subgroups	Parameters
[151] CO2	[306] CO2	151-155 184.15 0 0
[155] N2	[304] N2	155-151 80.825 0 0

Table of model results:

Name	ID	R	Q	Priv...	Version
CH2	1	0	1.2958		Delivery 2017
CH3	1	0	1.2958		Delivery 2017
CH2	2	0	0.9471		Delivery 2017
CH	3	0	0.2629		Delivery 2017
N2	155				Delivery 2017
N2	304	0	0.93		Delivery 2017
CO2	151				Delivery 2017
CO2	306	0	0.982		Delivery 2017
CH4	152				Delivery 2017
CH4	307	0	1.124		Delivery 2017

Hover the mouse on a cell of the matrix to display the group interaction parameters

If, for the selected model, the decomposition has not been provided for all the compounds, the following error is displayed:





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