Special Packages, Generalized Correlations and Association EOS

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Special Packages

Special Data Packages

- PRO/II has a number of thermodynamic methods specially developed for special industrial applications:
  - Alcohol Dehydration Systems (ALCOHOL)
  - Amines Package (AMINE)
  - Sour Water Packages (SOUR and GPSWATER)
  - Glycol Package (GLYCOL)

Alcohol Package (ALCOHOL)

- Alcohol package uses the NRTL method (uses same BIP's with NRTL method) to calculate phase equilibria. This package uses a special set of NRTL BIP's for alcohols, water and other components.

- Temperature:
  - 122 – 230 ^{o}F for H_2O-alcohol systems.
  - 150 – 230 ^{o}F for all other systems.

- Pressure: up to 1,500 psia

Alcohol Package (ALCOHOL)

- SRKM is used for the vapor enthalpy and density and the vapor and liquid entropy calculations.
- Ideal methods were used to estimate the liquid enthalpy and density calculations.
- Ideal liquid densities are obtained from pure-component saturated-liquid density correlations.
- Ideal liquid enthalpies are obtained from pure-component liquid enthalpy correlations and the corresponding vapor enthalpies are obtained by adding in the effect of the known latent heat of vaporization of the component.

Difference between Alcohol & NRTL Method

- Alcohol Package:
  - COMPONENT DATA
    LIBRARY ID 1,ETHANOL/2,WATER/3,BENZENE
    THERMODYNAMIC DATA
    METHOD SYSTEM=NRTL

- NRTL Method:
  - COMPONENT DATA
    LIBRARY ID 1,ETHANOL/2,WATER/3,BENZENE
    THERMODYNAMIC DATA
    METHOD SYSTEM=ALCOHOL

BIP's when using Alcohol Package

➤ ALCOHOL Package:

VLE LIQUID INTERACTION PARAMETERS FOR SET 'NRTL01'

NRTL BINARY COEFFICIENTS

I	J	A(I,J) / A(J,I)	B(I,J) / B(J,I)	C(I,J) / C(J,I)	ALPHAC / ALPHAT	UNITS FROM
1	2	0.498538	-456.0020	0.00	0.1448	DEG K SIMSCI VLEBANK
		1.015340	536.2640	0.00	0.0000	
1	3	-0.448518	440.5140	0.00	0.5355	DEG K SIMSCI VLEBANK
		-2.748070	1472.2400	0.00	0.0000	
2	3	3.611500	716.6600	0.00	0.2000	DEG K SIMSCI VLEBANK
		-5.803300	2933.8999	0.00	0.0000	

THERMOM Methods for Alcohol Package

➤ ALCOHOL Package:

```
THERMODYNAMIC METHODS USED FOR EACH SET

 THERMODYNAMIC SET          ALCO01 (DEFAULT)

   PROPERTY                 METHOD
   --------                 ------
   KVALUE(VLE)              ALCOHOL
   KVALUE(LLE)              UNSPECIFIED
   KVALUE(SLE)              UNSPECIFIED
   LIQUID ENTHALPY          IDEAL
   VAPOR  ENTHALPY          SRK-MODIFIED-PANAGIOTOPOULOS-REID
   LIQUID DENSITY           IDEAL
   VAPOR  DENSITY           SRK-MODIFIED-PANAGIOTOPOULOS-REID
   LIQUID ENTROPY           SRK-MODIFIED-PANAGIOTOPOULOS-REID
   VAPOR  ENTROPY           SRK-MODIFIED-PANAGIOTOPOULOS-REID
```

BIP's when using NRTL Method

➤ NRTL Method:

VLE LIQUID INTERACTION PARAMETERS FOR SET 'NRTL01'

NRTL BINARY COEFFICIENTS

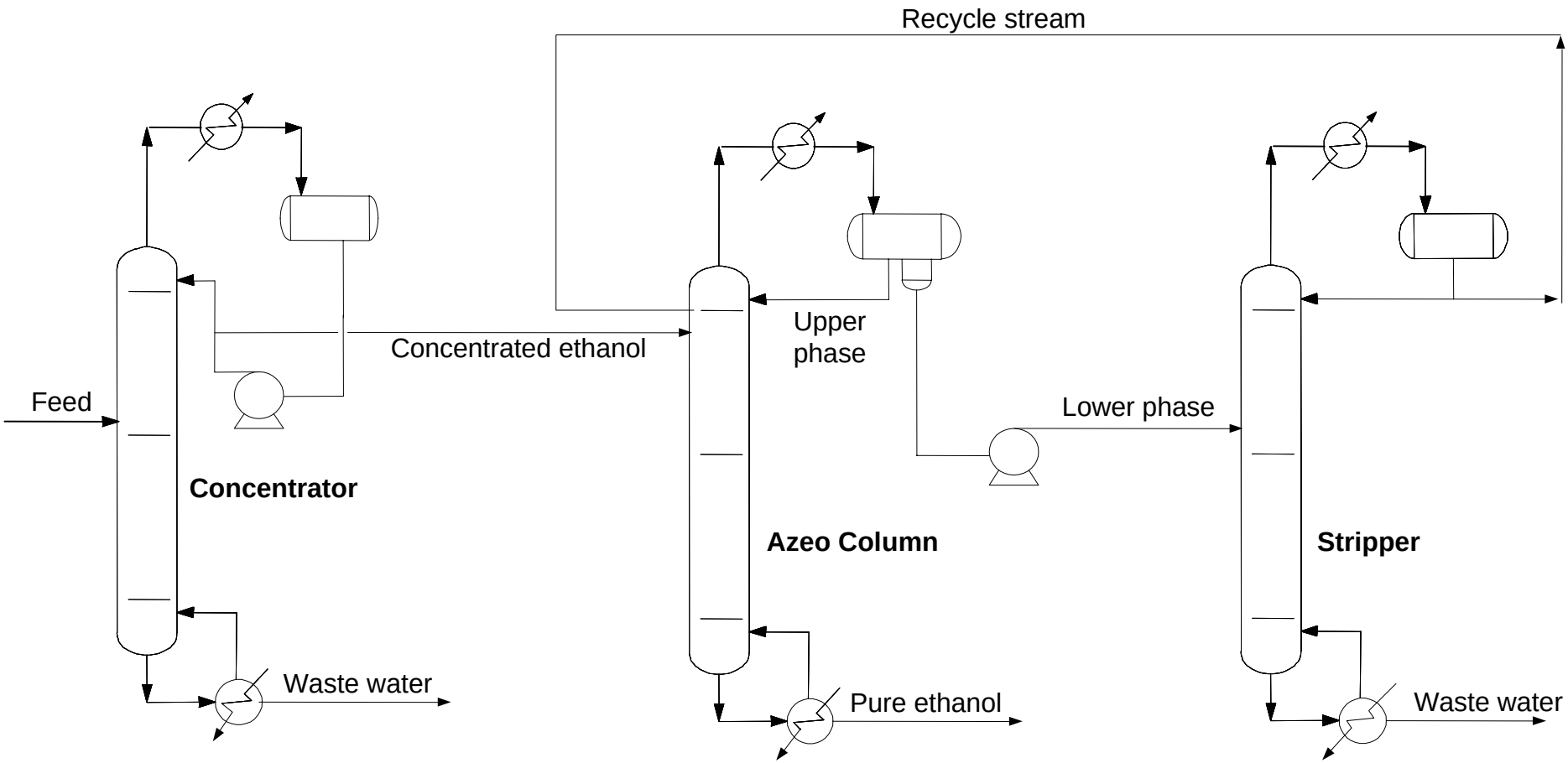
I	J	A(I,J) / A(J,I)	B(I,J) / B(J,I)	C(I,J) / C(J,I)	ALPHAC / ALPHAT	UNITS FROM
1	2	0.498538	-456.0020	0.00	0.1448	DEG K SIMSCI VLEBANK
		1.015340	536.2640	0.00	0.0000	
1	3	-0.448518	440.5140	0.00	0.5355	DEG K SIMSCI VLEBANK
		-2.748070	1472.2400	0.00	0.0000	
2	3	3.611500	716.6600	0.00	0.2000	DEG K SIMSCI VLEBANK
		-5.803300	2933.8999	0.00	0.0000	

THERMOM Methods for NRTL Method

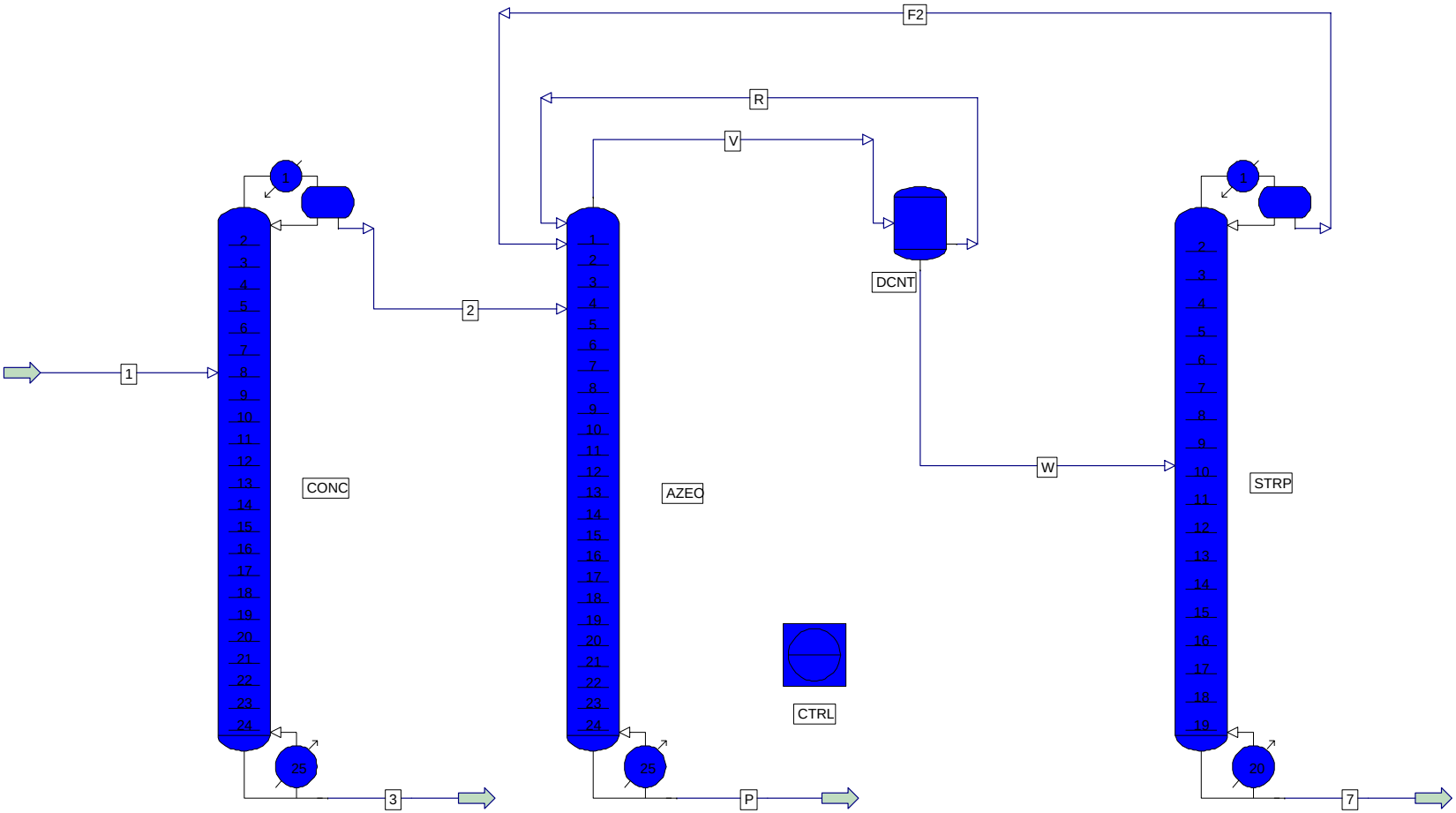
➤ NRTL Method:

```
THERMODYNAMIC METHODS USED FOR EACH SET

 THERMODYNAMIC SET          NRTL01 (DEFAULT)

   PROPERTY                 METHOD
   --------                 ------
   KVALUE(VLE)              NON-RANDOM-TWO-LIQUID
   KVALUE(LLE)              UNSPECIFIED
   KVALUE(SLE)              UNSPECIFIED
   LIQUID ENTHALPY          IDEAL
   VAPOR  ENTHALPY          IDEAL
   LIQUID DENSITY           IDEAL
   VAPOR  DENSITY           IDEAL
   LIQUID ENTROPY           UNSPECIFIED
   VAPOR  ENTROPY           UNSPECIFIED
```

Ethanol Dehydration using Entrainer



Example using PRO/II Alcohol Package



Amines

- Allows simulation of the treating of gas and liquid streams for the removal of H2S and CO2 using aqueous amines.
- The package has data for MEA, DEA, MDEA, DGA & DIPA.
- For MDEA and DGA, the effects of rate limitations can be simulated by applying an efficiency (we call RESIDENCE TIME FACTOR) to the equilibrium results.
- Based on the Kent-Eisenberg reaction equilibria model
- The package is not recommended for mixed amines.

Acid-base Chemical Equilibrium Reactions

- Water:

$$H_2O \overset{K_1}{\Leftrightarrow} H^+ + OH^-$$

- Hydrogen Sulfide:

$$H_2S \overset{K_2}{\Leftrightarrow} H^+ + HS^-$$

- Bi-sulfide:

$$HS^- \overset{K_3}{\Leftrightarrow} H^+ + S^{2-}$$

Acid-base Chemical Equilibrium Reactions

- Carbon Dioxide:

$$H_2O + CO_2 \overset{K_4}{\Leftrightarrow} H^+ + HCO_3^-$$

- Bicarbonate:

$$HCO_3^- \overset{K_5}{\Leftrightarrow} H^+ + CO_3^{2-}$$

- Alkanolamine:

$$RR'NH_2^+ \overset{K_6}{\Leftrightarrow} H^+ + RR'NH$$

Application Guidelines for Amine Systems

- For MEA and DEA systems, data have been regressed from a large number of sources, resulting in good prediction of phase equilibria for these systems.
- For systems containing DIPA, a limited amount of experimental data were available, and so the DIPA results are not recommended for final design purposes.
- The package is not recommended for mixed amines.

Application Guidelines for Amine Systems

- SRKM is used for the vapor enthalpy and density and the vapor and liquid entropy calculations.
- Ideal methods were used to estimate the liquid phase density calculations.
- The application ranges suggested for amine systems are shown in Table in next slide.

Application Guidelines for Amine Systems

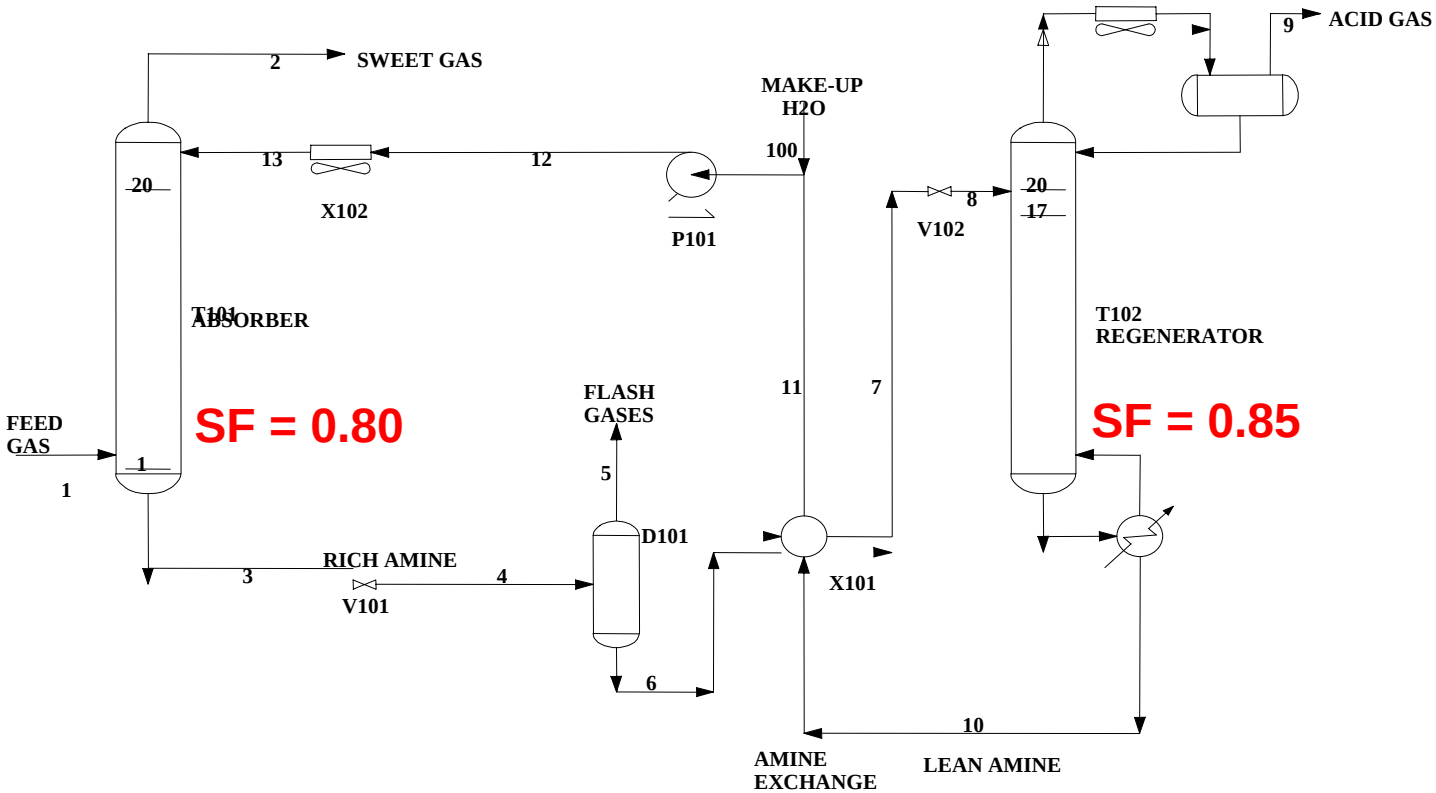
	AMINE				
	MEA	**DEA**	**DGA**	**MDEA**	**DIPA**
Pressure, psig	25-500	100 - 1000	100 - 1000	100 - 1000	100 - 1000
Temperature, ^{o}F	< 275	< 275	< 275	< 275	< 275
Concentratio, Wt% amine	~15 – 25	~25 – 35	~55 – 65	~50	~30
Acid gas loading, Gmole gas/gmole amine	0.5 – 0.6	0.45	0.50	0.4	0.4

THERMOM Methods for AMINE Package

➤ AMINE Package:

```
THERMODYNAMIC METHODS USED FOR EACH SET

 THERMODYNAMIC SET          AMIN01 (DEFAULT)

   PROPERTY                 METHOD
   --------                 ------
   KVALUE(VLE)              AMINE SYSTEM
   KVALUE(LLE)              UNSPECIFIED
   KVALUE(SLE)              UNSPECIFIED
   LIQUID ENTHALPY          AMINE SYSTEM
   VAPOR  ENTHALPY          SRK-MODIFIED-PANAGIOTOPOULOS-REID
   LIQUID DENSITY           IDEAL
   VAPOR  DENSITY           SRK-MODIFIED-PANAGIOTOPOULOS-REID
   LIQUID ENTROPY           SRK-MODIFIED-PANAGIOTOPOULOS-REID
   VAPOR  ENTROPY           SRK-MODIFIED-PANAGIOTOPOULOS-REID
```

Sour Gas Removal using Aqueous Amine



Sour Water Systems

- PRO/II has 2 sour water methods available:
  - SOUR
  - GPSWAT
- SOUR
  - Based on the SWEQ (Sour Water EQuilibrium) model developed by Grant Wilson for the API/EPA.
  - Contains the 4 sour components: (H2O, NH3, H2S, CO2)
  - Based on correlations of the sour component partial pressures.

Sour Water Systems

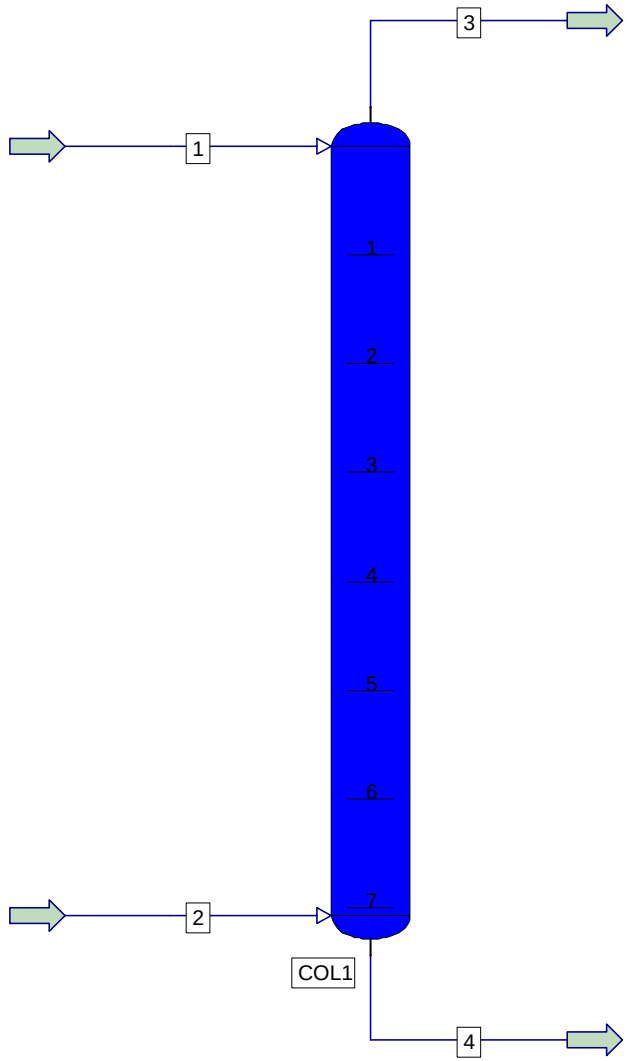
- GPSWAT
  - Based on the GPSWAT model developed by Grant Wilson for the GPA.
  - Contains 19 components, including the 4 sour components: (H2O, NH3, H2S, CO2)
  - It is a rigorous model of the reactive equilibria in the system.

Sour Water Systems

- Both Methods:
  - Both methods can be used for rigorous VLLE calculations .
  - Both methods can be used with petroleum fractions.

Difference between SOUR and GPSAWATER

Feed Stream Information	
Feed Component	Composition (lb/hr)
N2	2.000
CH4	3.000
H2S	795.654
NH3	810.560
CO2	5.000
HCN	0.238
NC6	0.595
NC9	0.430
H2O	25,584.713
Temperature (F)	150
Pressure (psia)	25



Keyword Input for Sour Water Stripper

- SOUR:
  - THERMODYNAMIC DATA

```
METHOD KVAL(VLE)=SOUR,ENTH(L)=IDEAL,&
 ENTH(V)=SRKM,DENS(L)=IDEAL,&
 DENS(V)=SRKM
```

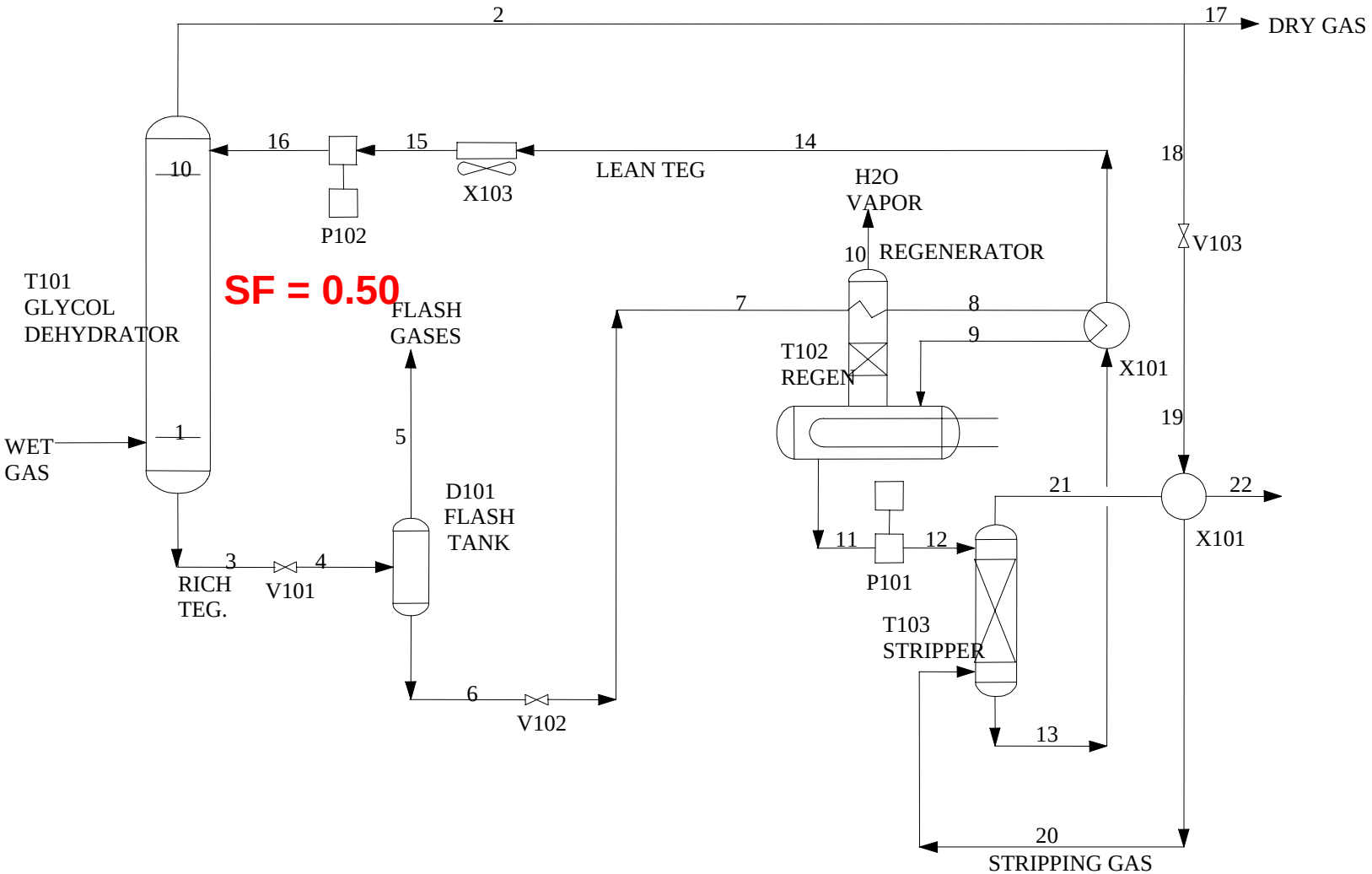
- GPSWATER:
  - THERMODYNAMIC DATA

```
METHOD KVAL(VLE)=GPSWAT,ENTH(L)=IDEAL,&
 ENTH(V)=SRKM,DENS(L)=IDEAL,&
 DENS(V)=SRKM
```

Glycol Dehydration (GLYCOL Package)

- Natural gas dehydration with Triethylene Glycol (TEG).
- Uses the SRKM equation of state.
- Rigorously models either VLE or VLLE behavior.
- T range: 80 ^{o}F to 400 ^{o}F.
  P range: Up to 2000 psia.
- Glycol (EG, DEG, TEG or TTEG) and water must be present.

Gas Dehydration using TEG



Application Guidelines

Hydrocarbon Systems (I)

- Refining Processes
  - Grayson-Streed: H2-rich Systems, CDU, VDU, Coker Fractionator, FCC Main Fractionator
  - SRK, PR : Lightends Columns, Splitters, GCR
  - SOUR: Sour Water Systems
  - SRKKD, SRKM, SRKS : Use if HC Solubility in Water (VLLE) is important.
  - Based on the GPSWAT model developed by Grant Wilson for the GPA.

Hydrocarbon Systems (II)

- Gas Processes
  - SRK, PR : All types of gas processing plants including cryogenic systems
  - SRKM, PRM : Systems with water, CO2 and other polar components (Check BIP's.)
  - GLYCOL : Dehydration with TEG.
  - AMINE : Natural Gas Sweetening.
  - SRKKD, SRKM, SRKS : Use if light gas. solubility in water (VLLE) is important.
  - Grayson-Streed: H2-rich Systems, CDU, VDU, Coker Fractionator

Chemical Systems (LACT Models)

- Gas Processes
  - Non-ideal components (Liquid phase)
  - Low to moderate pressure about up to 10 bar
  - Rely on binary interaction parameters strongly (if parameters are missing, the results will be close to ideal !)
  - Missing parameters can be estimated from structures.
  - Used with Henry's law option for non condensibles (supercritical gases).
  - VLLE with some methods

The End of General Thermodynamics

The End….