

458.401 Process & Product Design

13

Synthesis of a Process Using a Simulator and Simulator Troubleshooting

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Simulator Troubleshooting

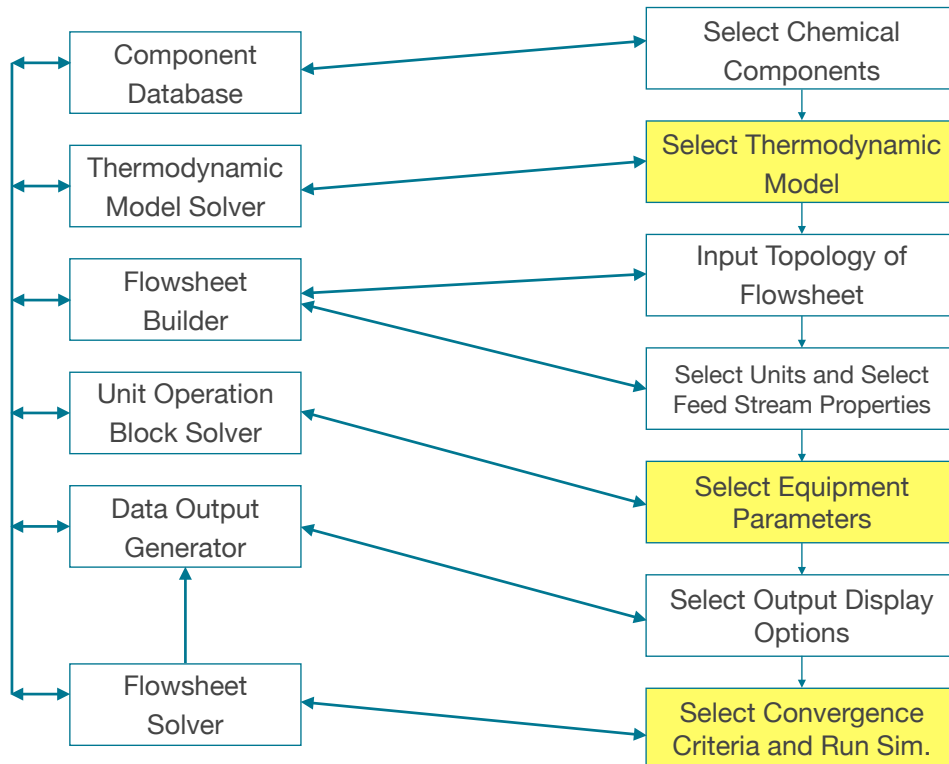
Introduction

- A process simulator typically handles batch, semi-batch, and continuous processes
- Blind use of simulators can be potentially dangerous
- This lecture emphasizes the **general** approach to setting up processes and
- Highlights some of the common problems that process simulator users encounter and offers solutions to these problems

Structure of Process Simulator

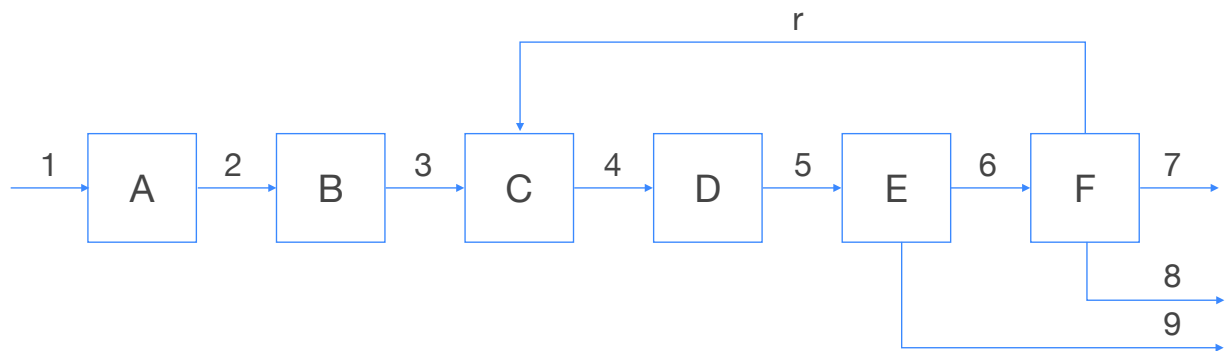
Basic Computational Elements
in Process Simulator

Sequence of Input Steps for a
Simulation Problem

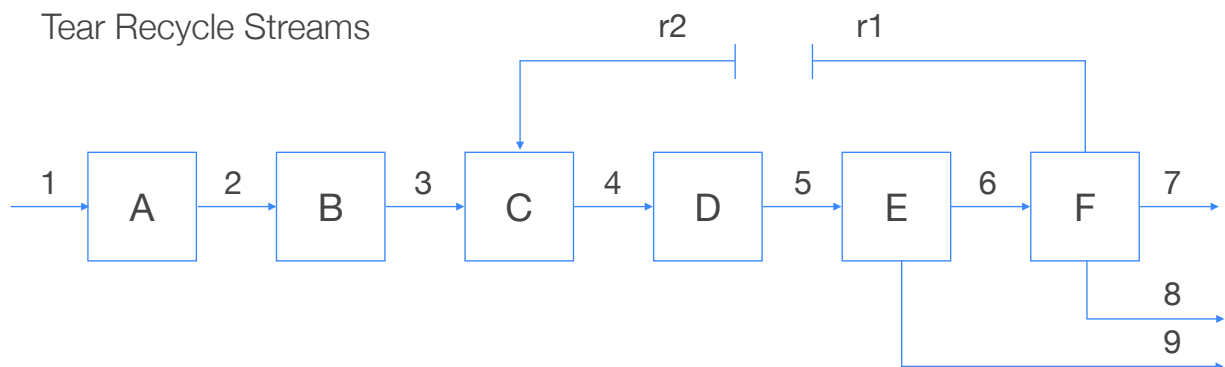


Sequential Modular Approach

- Groups the equations describing the performance of equipment units and solves them in modules
- Most widely used, e.g., Aspen Plus
- Each piece of equipment is solved in sequence
- The output from a given piece of equipment, along with specific information on the equipment, becomes the input to the next piece of equipment
- For a process with recycle streams, tearing of recycle streams and iterations are involved



Tear Recycle Streams



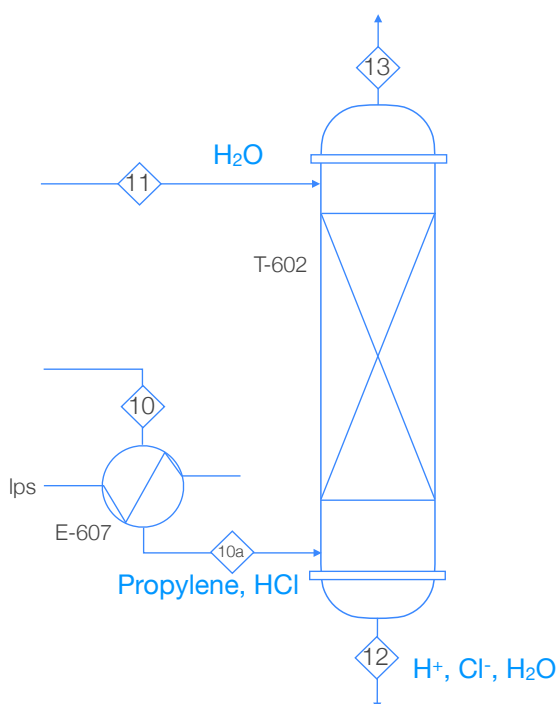
Input Data: Chemical Components

- Simulators will have a databank of many components
- All components (inerts, reactants, products, by-products, utilities, and waste chemicals) should be identified
- Chemicals unavailable in the databank can be added (user-added components)

Input Data: Physical Property Model

- Simulators use both pure component and mixture properties
 - viscosity, thermal conductivity, diffusivity, enthalpy, fugacity, K-factors, critical constants, density, M.W., surface tension, etc.
- Expert systems to help the user select the appropriate model
 - But, not recommended
- A moderately complex simulation will use at least two different thermodynamic packages for different parts of the flowsheet

Example 13.1 HCl absorber (T-602)



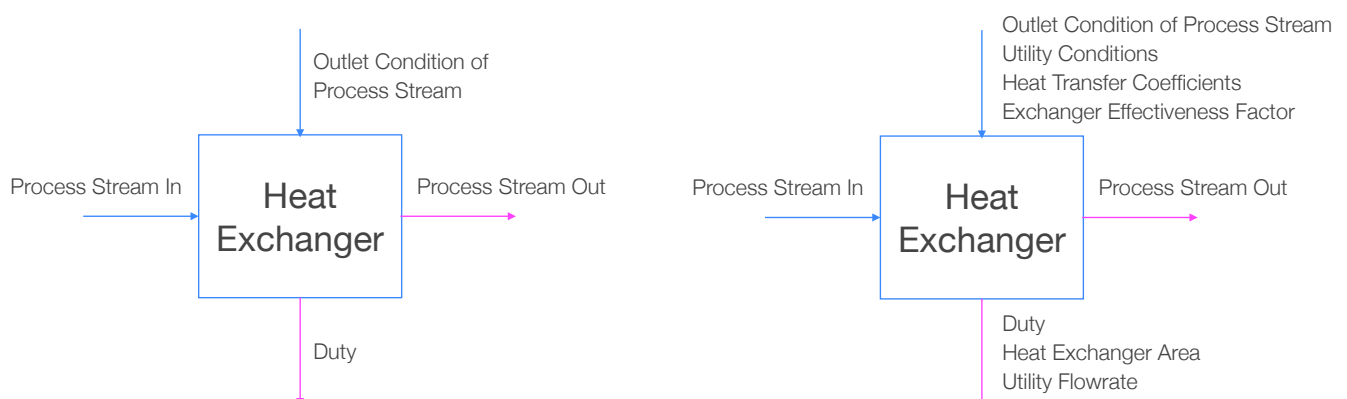
Phase Component Flows (kmol/h)	SRK Model		PPAQ Model	
	Stream 12 Liquid	Stream 13 Vapor	Stream 12 Liquid	Stream 13 Vapor
Propylene	0.05	57.48	—	57.53
Ally Chloride	0.01	—	0.01	—
Hydrogen Chloride	0.91	18.78	19.11	0.58
Water	81.37	0.63	81.88	0.12
Total	82.34	76.89	101.00	58.23

Input Data: Topology and Feed Stream

- Selection and Input of Flowsheet Topology
 - Every time a stream splits or several streams combine, a simulator equipment module (splitter or mixer) must be included
 - Care must be taken when connecting batch and continuous unit operations
- Feed Stream Properties
 - Feed with n components, 1 or 2 phases: $n + 2$ specifications
 - If the feed is a single component and contains 2 phases
 - ▶ T and P are not independent
 - ▶ Vapor fraction (vf) and T or P are specified
 - Vf can be used to specify a **two-phase multicomponent** system, but **not recommended**
 - Use the vf to define feed stream only for **saturated vapor** ($vf = 1$), **saturated liquid** ($vf = 0$), and **two-phase, single-component** ($0 < vf < 1$) streams; **All other streams should be specified using the T and P**

Input Data: Equipment Parameters

- Level 1 Simulation
 - Minimum data are supplied to solve material and energy balances
- Level 2 Simulation
 - Do as many of the design calculations as possible; more input data than Level 1



Input Data: Equipment Parameters

- Pumps
 - Desired P of the fluid leaving the pump or desired $+\Delta P$
- Compressors and Turbines
 - Desired P of the fluid leaving the pump or desired $+\Delta P$
 - Mode of compression or expansion: adiabatic, isothermal, or polytropic
- Heat Exchangers
 - Single process stream, Fired Heaters
 - ▶ Exit process stream (exit P and T - single phase exit condition or exit P and v_f - two phase exit condition)
 - Two or multiple process streams (e.g., heat integration)
 - ▶ Exit conditions for both streams
 - ▶ Be aware of the possibility of temperature crosses: check the T profiles

Input Data: Equipment Parameters

- Mixers: simple tees in pipes
 - Outlet pressure or pressure drop at the mixing point (very small)
 - If feed streams enter the mixer at different pressures, the outlet stream is assumed to be at the lowest pressure of the feed streams (little error in MEBs) — correct analysis in Section 22.4
- Splitters
 - Outlet pressure or pressure drop across the device
 - Relative flows of the output streams
- Valves
 - Either the outlet pressure or pressure drop

Input Data: Equipment Parameters

- Reactors
 - Stoichiometric Reactor
 - ▶ # and stoichiometry of the reactions, T, P, conversion of the limiting reactant
 - ▶ Reactor configuration (PFR, CSTR) is not required because no estimate of reactor volume is made. Only basic MEBs are performed
 - Kinetic (Plug Flow and CSTR) Reactor
 - ▶ Kinetic expressions are known
 - ▶ # and stoichiometry of the reactions,
 - ▶ Kinetic constants (Arrhenius rate constants, Langmuir-Hinshelwood, etc.), and
 - ▶ Reactor configuration (PFR, CSTR) is required
 - ▶ Cooling and heating of reactants may be available to generate T profiles in the reactor

Input Data: Equipment Parameters

- Reactors
 - Equilibrium Reactor
 - ▶ # and stoichiometry of the reactions and
 - ▶ Fractional approach to equilibrium are required
 - ▶ Equilibrium constants as $f(T)$ may be required for each reaction or may be calculated directly from information in the DB
 - Minimum Gibbs Free Energy Reactor
 - ▶ Another common form of the equilibrium reactor
 - ▶ Outlet stream composition is calculated by a free energy minimization technique
 - ▶ Usually data are available from the DB
 - ▶ The only input data: list of components that one anticipates in the output from the reactor
 - ▶ Equilibrium conversion: infinite residence time

Input Data: Equipment Parameters

- Reactors
 - Batch Reactor
 - ▶ Similar to kinetic reactor (requires the same kinetic input)
 - ▶ The volume of the reactor is specified
 - ▶ The feeds, outlet flows, and reactor T (or heat duty) are scheduled (i.e., specified as time series)
- Which reactor to choose?
 - Start with the least complicated reactor that will allow the heat and material balance to be established
 - The reactor module can always be substituted later with a more complex one
 - Make sure you choose a correct _____ reactant when specifying a desired conversion

Input Data: Equipment Parameters

- Flash Units: single-stage VLE calculation
 - In order to specify completely condition of the two output streams (liquid and vapor), two parameters must be input
 - Many possible combinations
 - ▶ T and P, T and heat load, or P and mole ratio of vapor to liquid in exit streams
 - The flash module is a combination of two pieces of physical equipment: phase separator and heat exchanger
 - Can serve as a surge or storage vessel for batch operation

Input Data: Equipment Parameters

- Distillation Column
 - Rigorous methods: _____ calculations
 - Shortcut methods: Fenske and Underwood relationships using key components
 - ▶ DSTWU (Aspen Plus)
 - Winn method for $N_{\min}$
 - Underwood method for $R_{\min}$
 - Gilliland to relate actual # of stages and RR
 - Use shortcut first to get preliminary design calculations
 - In both methods, duties of the reboiler and condenser are carried out. Detailed design of these heat exchangers (area calculations) often cannot be carried out during the column simulation

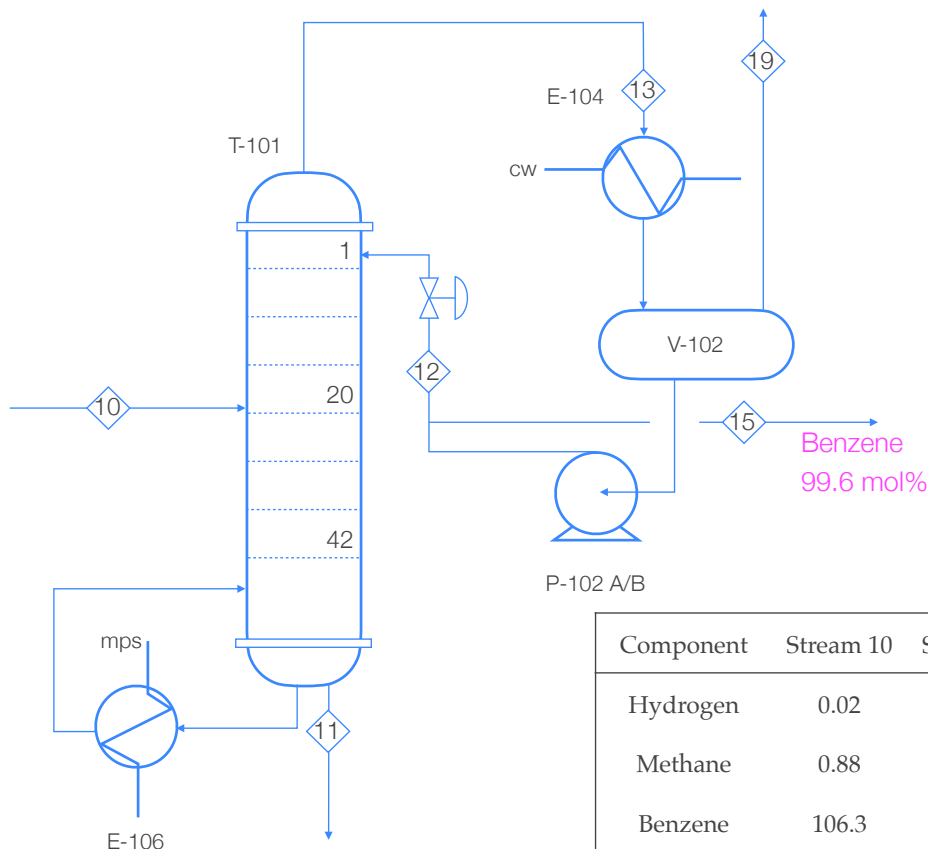
Input Data: Equipment Parameters

- Distillation Column: Shortcut (e.g., DSTWU in Aspen Plus)
 - Inputs
 - ▶ Identification of the key components to be separated
 - ▶ Fractional recoveries of each key component in the overhead product
 - ▶ Column pressure and pressure drop
 - ▶ The ratio of actual to minimum reflux ratio
 - The simulator will estimate the number of theoretical plates required, the exit stream conditions (bottom and overhead products), optimum feed location, and the reboiler and condenser duties

Input Data: Equipment Parameters

- Distillation Column: Rigorous (e.g., RADFRAC in Aspen Plus)
 - Inputs: total # of specs = # of products (top, bottom, and side streams)
 - ▶ # of theoretical plates
 - ▶ Condenser and reboiler type
 - ▶ Column pressure and pressure drop
 - ▶ Feed tray location and side product locations (if needed)
 - Tray-to-tray equilibrium calculations can be handled for several hundred stages
 - This can be used to simulate accurately other equilibrium staged devices, for example, absorbers and strippers
- Batch distillation: similar to the rigorous module, except that feeds and product draws are on a schedule

Example 13.2 Benzene Recovery Column



Component	Stream 10	Stream 15	Stream 19	Stream 11
Hydrogen	0.02	—	0.02	—
Methane	0.88	—	0.88	—
Benzene	106.3	105.2	—	1.1
Toluene	35.0	0.4	—	34.6

Specification 1

Key components: Benzene and Toluene

Top composition: Benzene 99.6 mol%

Recovery of toluene in the bottoms is 0.98

Violates the MB

Specification 2

Top composition: Benzene 99.6 mol%

Recovery of benzene in the bottoms is 0.01

Do not violate
the MB

Make sure your specifications do not violate the MB

Input Data: Equipment Parameters

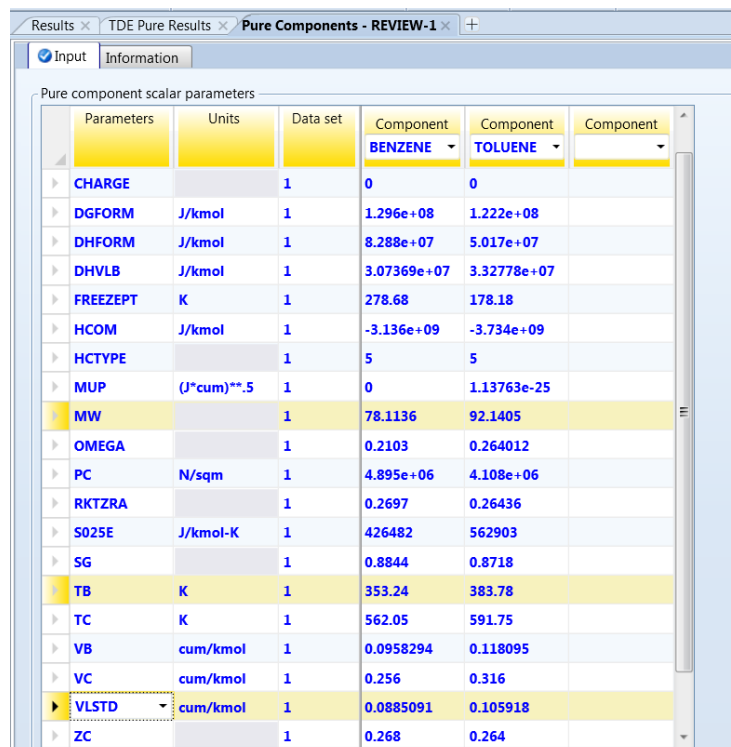
- Absorbers and Strippers
 - Usually simulated using the rigorous distillation module
 - Condensers and reboilers are not normally used
 - Two feeds
- Liquid-Liquid Extractors
 - A rigorous tray-by-tray module is used to simulate this multistage equipment
 - Thermodynamic model for two liquid phases (appropriate liquid-phase activity coefficients)

Three Common Causes for Divergence

- Ill-posed problem. This normally means that an equipment **specification has been given incorrectly**.
- Too tight tolerance
- The number of iterations is not sufficient for convergence. This occurs most often with many recycle streams.
 - Remove as many recycle streams as possible and add the recycle streams back, one by one, using the results from the preceding simulation as the starting point for the new one. (Read 13.3)

Physical Properties Estimation - Pure Component Properties

- 3 Most Fundamental **Fixed** Properties
 - Molecular weight
 - Standard liquid density
 - Normal boiling point
- Benzene, Toluene



Parameters	Units	Data set	Component BENZENE	Component TOLUENE	Component
CHARGE		1	0	0	
DGFORM	J/kmol	1	1.296e+08	1.222e+08	
DHFORM	J/kmol	1	8.288e+07	5.017e+07	
DHVLB	J/kmol	1	3.07369e+07	3.32778e+07	
FREEZEPT	K	1	278.68	178.18	
HCOM	J/kmol	1	-3.136e+09	-3.734e+09	
HCTYPE		1	5	5	
MUP	(J*cum)**.5	1	0	1.13763e-25	
MW		1	78.1136	92.1405	
OMEGA		1	0.2103	0.264012	
PC	N/sqm	1	4.895e+06	4.108e+06	
RKTZRA		1	0.2697	0.26436	
S02SE	J/kmol-K	1	426482	562903	
SG		1	0.8844	0.8718	
TB	K	1	353.24	383.78	
TC	K	1	562.05	591.75	
VB	cum/kmol	1	0.0958294	0.118095	
VC	cum/kmol	1	0.256	0.316	
VLSTD	cum/kmol	1	0.0885091	0.105918	
ZC		1	0.268	0.264	

Pure Component Properties - Critical Point

What is a critical point?

A maximum point at which vapor and liquid phases coexist with each other

Gas vs. Vapor

Gas: H₂, O₂, N₂, CO, CO₂, or CH₄

(임계점이 매우 낮은 온도, 일반 온도에서 대부분 초임계 상태. 기상-액상 공존 X)

Vapor (증기 - 증발된 기체): Water, Benzene, Toluene, Xylenes, ...

액상이 base에 있어야 함

임계압축인자

$$Z_c = \frac{v^{\text{real}}}{v^{\text{ideal}}} = \frac{p_c v_c}{RT_c}$$

Critical Properties of CO₂

T_c: 304.21 K

P_c: 7,383 kPa

V_c: 0.094 m³/kmol

Z_c: 0.274

Pure Components - REVIEW-1				
Input Information				
Pure component scalar parameters				
Parameters	Units	Data set	Component	Component
			CO2	
HCTYPE		1		
MUP	(J*cum)**.5	1	0	
MW		1	44.0098	
OMEGA		1	0.223621	
PC	kPa	1	7383	
RKTZRA		1	0.27256	
S025E	J/kmol-K	1	210887	
SG		1	0.3	
TB	K	1	194.7	
TC	K	1	304.21	
VB	cum/kmol	1	0.0350189	
VC	cum/kmol	1	0.094	
VLSTD	cum/kmol	1	0.0535578	
ZC		1	0.274	
DCPLS	J/kmol-K	1	14258.4	
DHAQFM	J/kmol	1	-4.138e+08	
HFUS	J/kmol	1	9.019e+06	
OMGPRS		1	0.231	
PCPRS	N/sqm	1	7.376e+06	
TCPRS	K	1	304.15	

Example-01

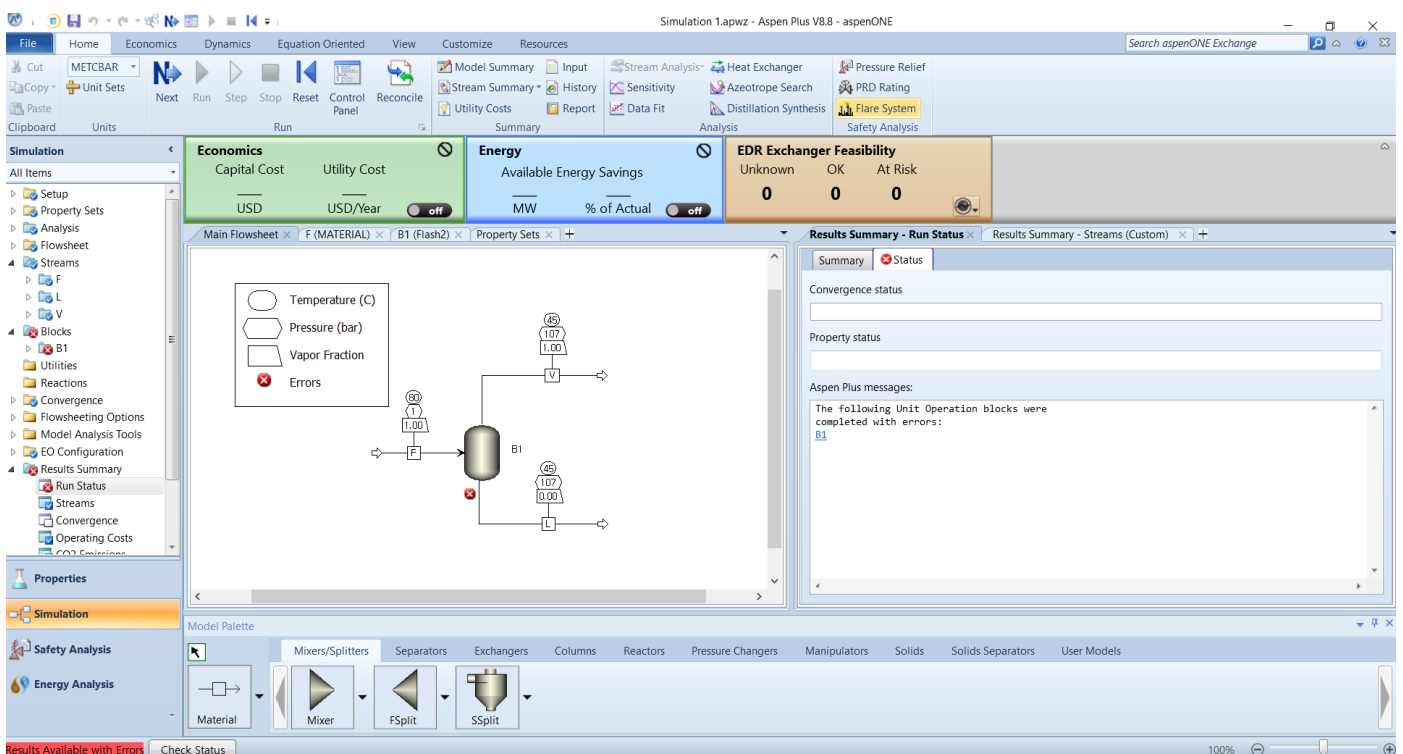
Estimated overhead vapor product compositions at column top are: CH_4 65 mol%, C_2H_6 15 mol%, C_3H_8 15 mol%, and $\text{i-C}_4\text{H}_{10}$ 5 mol%

If reflux drum operating temperature is 45°C , estimate reflux drum operating pressure. Use Peng-Robinson EOS model for your simulation

If you cannot get a converged solution, explain the reason

Estimate pseudo critical temperature for the above 4 component mixture

Peng-Robinson



Simulation 1.apwz - Aspen Plus V8.8 - aspenONE

File Home Economics Dynamics Equation Oriented View Customize Resources

Simulation Economics Utility Cost Energy EDR Exchanger Feasibility

Capital Cost USD USD/Year off Available Energy Savings MW % of Actual off

Unknown OK At Risk 0 0 0

Results Summary - Run Status

Summary Status

Convergence status

Property status

Aspen Plus messages:

The following Unit Operation blocks were completed with errors:

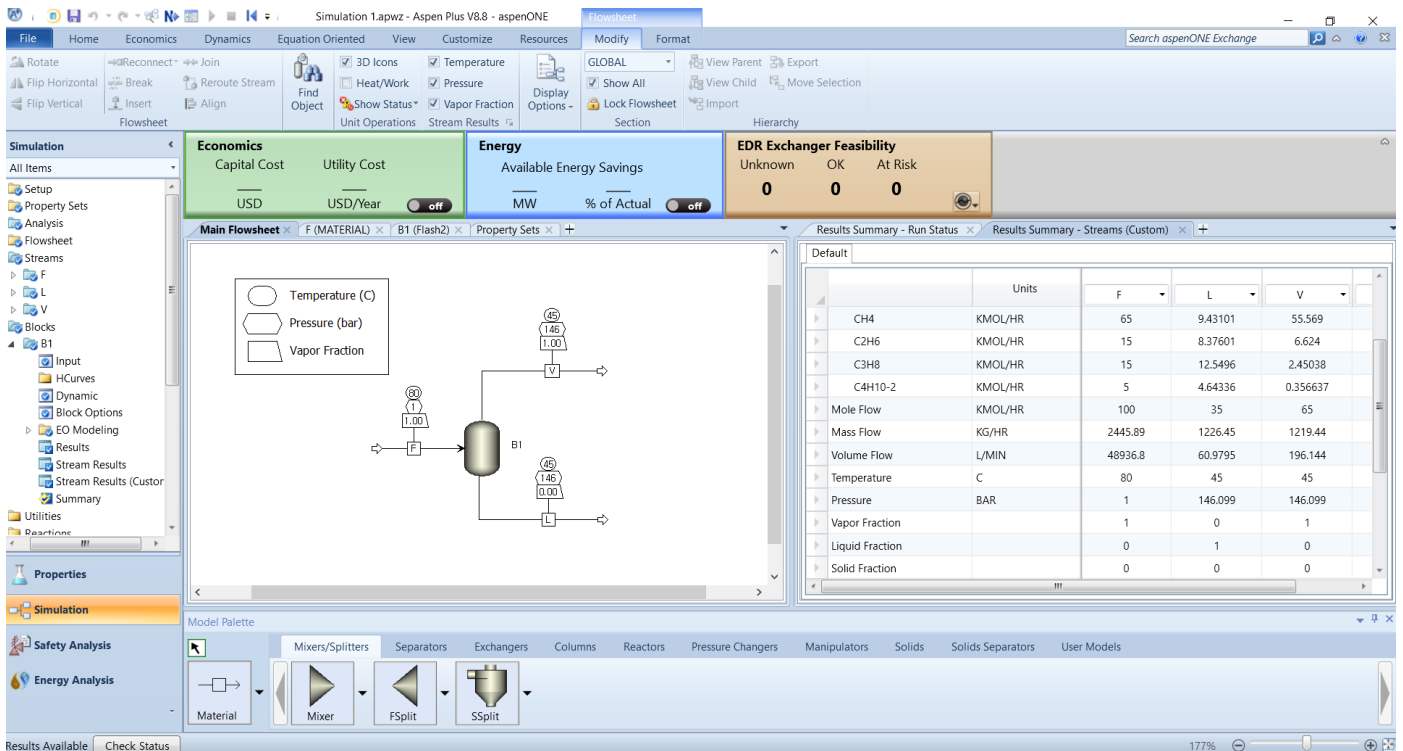
B1

Model Palette

Mixers/Splitters Separators Exchangers Columns Reactors Pressure Changers Manipulators Solids Solids Separators User Models

Material Mixer FSplit SSplit

Results Available with Errors Check Status 100%

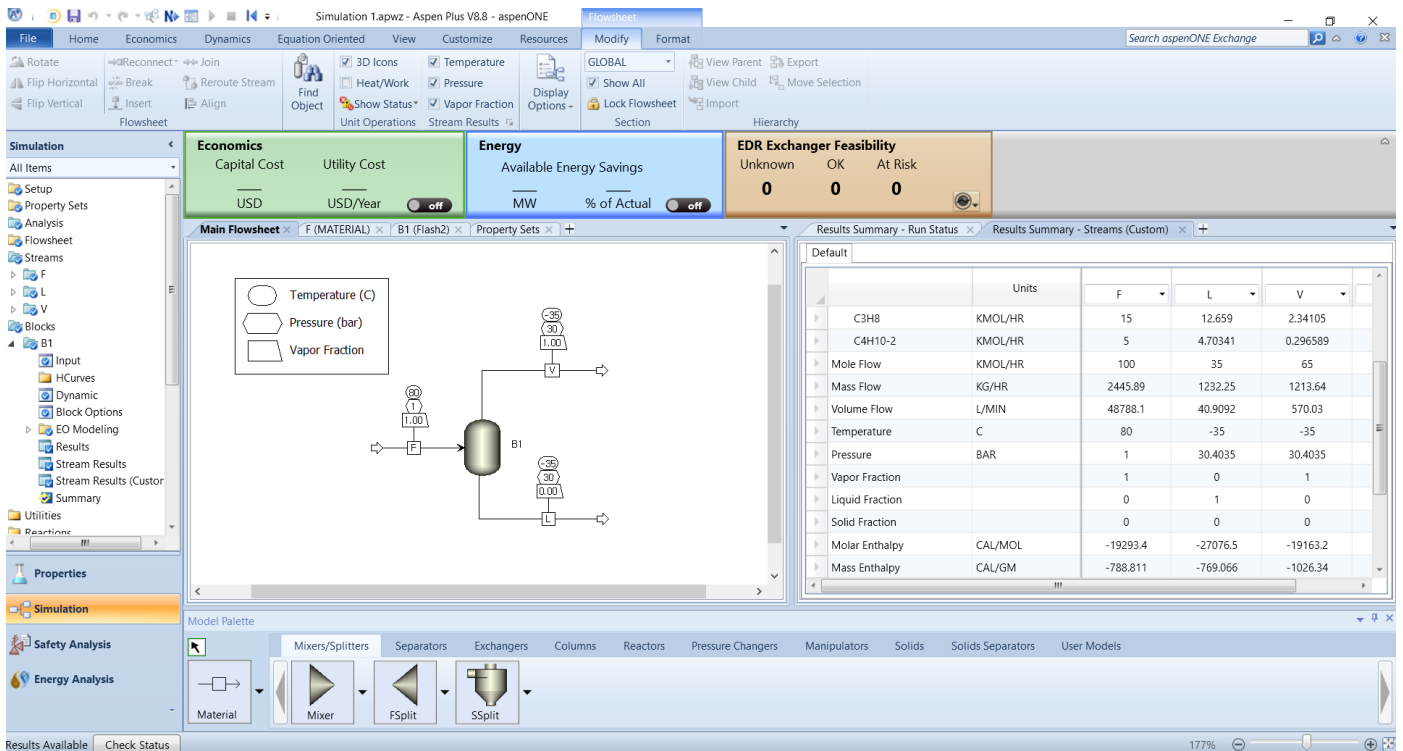


Components	Tc [°C]	Mole Fraction
C1	-82.59	0.65
C2	32.17	0.15
C3	96.68	0.15
iC4	134.99	0.05
Tcm	-27.61	

Pseudo Critical Temperature = -27.6039 °C

Pseudo Critical Pressure = 45.3975 bar

Peng-Robinson with -35°C



Pure Component Properties

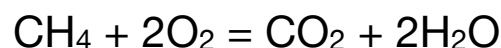
Standard heat of reaction from heat of formation

Heats of formation

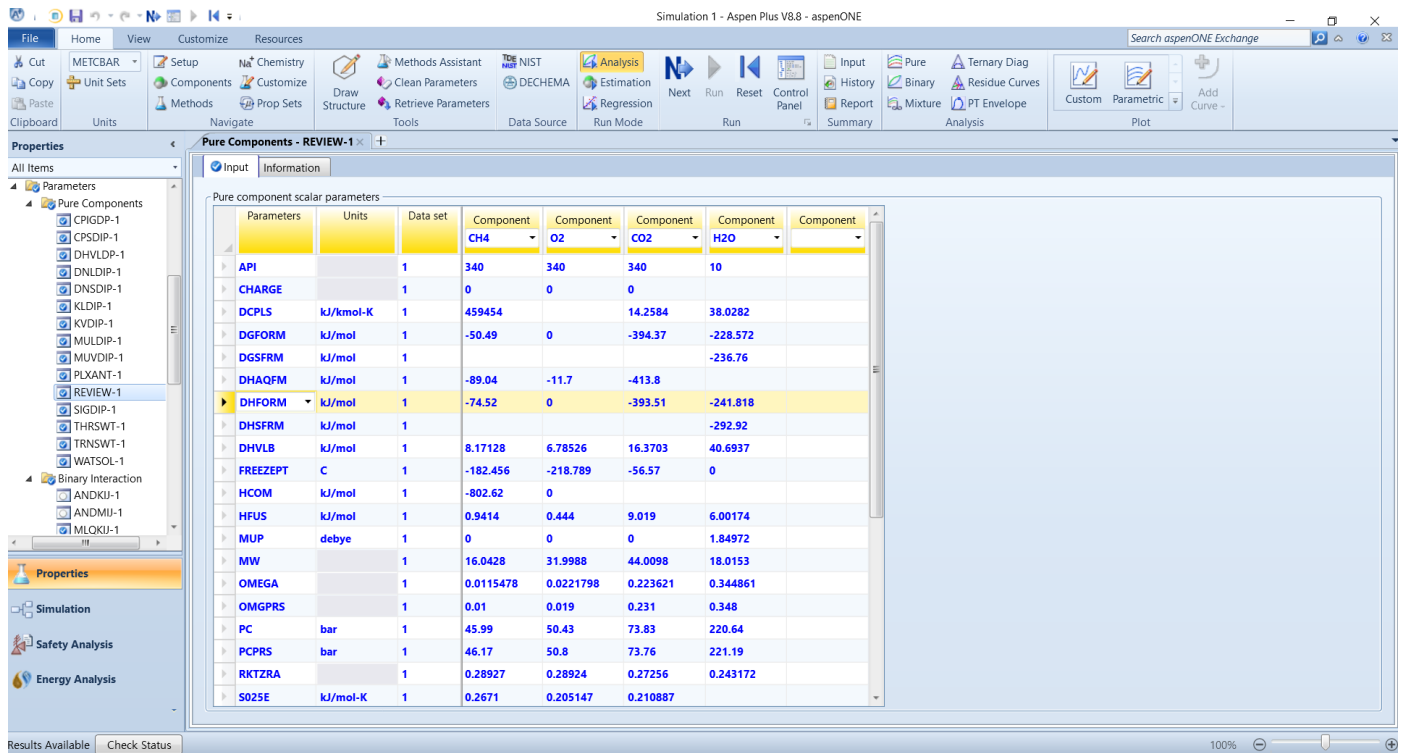
Enthalpy of formation: Standard heat of formation

Gibbs free energy of formation

From the standard heat of formation of each component, estimate standard heat of reaction



Heat of Formation



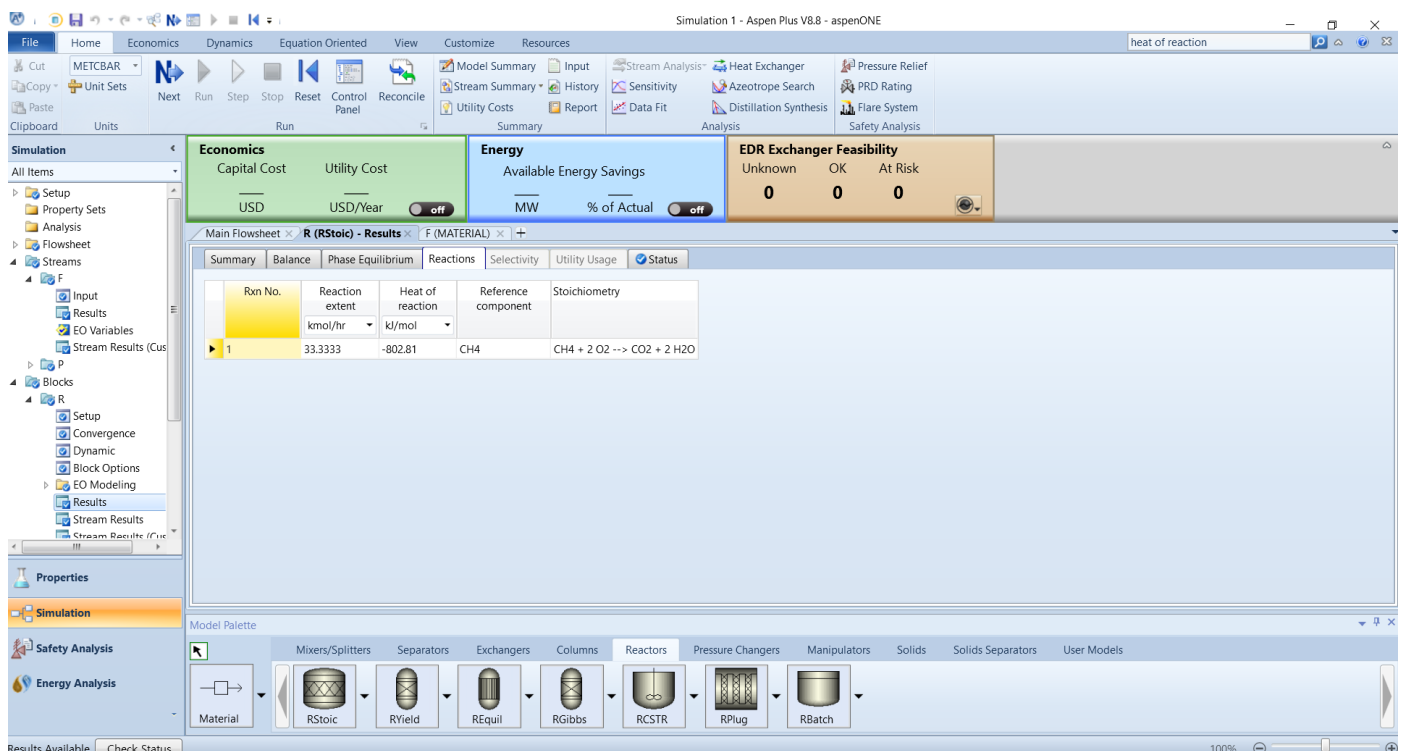
Simulation 1 - Aspen Plus V8.8 - aspenONE

Pure Components - REVIEW-1

Pure component scalar parameters

Parameters	Units	Data set	Component	Component	Component	Component	Component
			CH4	O2	CO2	H2O	
API		1	340	340	340	10	
CHARGE		1	0	0	0		
DCPLS	kJ/kmol-K	1	459454		14.2584	38.0282	
DGFORM	kJ/mol	1	-50.49	0	-394.37	-228.572	
DGSFRM	kJ/mol	1				-236.76	
DHAQFM	kJ/mol	1	-89.04	-11.7	-413.8		
DHFORM	kJ/mol	1	-74.52	0	-393.51	-241.818	
DHSFRM	kJ/mol	1				-292.92	
DHVLB	kJ/mol	1	8.17128	6.78526	16.3703	40.6937	
FREEZEPT	C	1	-182.456	-218.789	-56.57	0	
HCOM	kJ/mol	1	-802.62	0			
HFUS	kJ/mol	1	0.9414	0.444	9.019	6.00174	
MUP	debye	1	0	0	0	1.84972	
MW		1	16.0428	31.9988	44.0098	18.0153	
OMEGA		1	0.0115478	0.0221798	0.223621	0.344861	
OMGPRS		1	0.01	0.019	0.231	0.348	
PC	bar	1	45.99	50.43	73.83	220.64	
PCPRS	bar	1	46.17	50.8	73.76	221.19	
RKTZRA		1	0.28927	0.28924	0.27256	0.243172	
S02SE	kJ/mol-K	1	0.2671	0.205147	0.210887		

Heat of Reaction



Simulation 1 - Aspen Plus V8.8 - aspenONE

heat of reaction

Economics

Capital Cost

Utility Cost

USD

USD/Year

Energy

Available Energy Savings

MW

% of Actual

EDR Exchanger Feasibility

Unknown OK At Risk

0 0 0

Main Flowsheet R (RStoic) - Results F (MATERIAL)

Summary Balance Phase Equilibrium Reactions Selectivity Utility Usage Status

Rxn No.	Reaction extent	Heat of reaction	Reference component	Stoichiometry
	kmol/hr	kJ/mol		
1	33.3333	-802.81	CH4	CH4 + 2 O2 -> CO2 + 2 H2O

Model Palette

Mixers/Splitters Separators Exchangers Columns Reactors Pressure Changers Manipulators Solids Solids Separators User Models

Material RStoic RYield REquil RGibbs RCSTR RPlug RBatch

Component	ΔH_f [kJ/kmol]
CH ₄	-74,520
O ₂	0
CO ₂	-393,510
H ₂ O	-241,810
	ΔH_R^0 (25°C)
CH ₄ + 2O ₂ = CO ₂ + 2H ₂ O	-802,610

Physical Properties Estimation - Pure Component Properties

- **Temperature-Dependent Properties** (열역학적 물성)
 - Vapor pressure (liquid phase property)
 - Enthalpy (열함량) for gas, liquid, and solid
 - Idea gas heat capacity (열용량, 비열) (function of temperature)
 - Heat of vaporization (증발 잠열)
 - Densities for gas, liquid, and solid
- **Transport Properties** (전달 물성)
 - Viscosity, thermal conductivity, diffusion coefficient, surface tension (역시 온도 의존)

Vapor Pressure (액체의 증기압)

- Method 1: Clausius-Clapeyron Equation

$$\ln \left(\frac{P^{vap}}{P^0} \right) = \frac{\Delta H^{vap}}{R} \left(\frac{1}{T} - \frac{1}{T^b} \right)$$

- Method 2: Equation of state - ω (acentric factor) or Twu's Alpha Function 이용
- Method 3: Antoine Equation (매개변수 개수가 simulator에 따라 다를 수 있음)

Choosing Thermodynamic Model

- If T_c and P_c are known for each pure component, the parameters for simple, cubic equations of state can be estimated.
- Pure-Component Properties
 - Density, viscosity, thermal conductivity, and heat capacities are generally available in simulator.
 - GCM is reasonably good for estimation
- Enthalpy
 - Although the pure-component heat capacities are calculated with acceptable accuracy, the enthalpies of phase changes often are not.
 - If ΔH_{vap} is an important part of a calculation, simple EOS should not be used. In fact, "latent heat" or "ideal" options would be better.
 - If the substance is above or near its T_c , EOS must be used. However, the user must beware, especially if polar substances such as water are present

Example 13.3

A gas stream at 3000°F of the following concentration is to be cooled by evaporation of 500 kg/h of water entering at 70°F. Assume atmospheric pressure

H ₂	22.72 kg/h
N ₂	272.24
CO	268.40
HCl	26.84

Perform a simulation to determine the final temperature of the cooled gas stream with the default thermodynamic model and with the ideal model.

PR or SRK gives an outlet temp of 480°F. The ideal model gives an outlet temp of 348°F. The value calculated by the ideal model is closer to reality in this case because the EOS do a poor job of estimating the enthalpy of vaporization of water, which is the most important property for the energy balance.

The ideal model uses the **experimentally determined value of this enthalpy** of vaporization (from the DB)

Phase Equilibria

- PE is sometimes called the fugacity coefficient, K-factor, or fluid model.
- Whenever possible, **phase-equilibrium data** should be used to **regress the parameters** in the model, and the deviation between the model predictions and the experimental data should be studied.
- EOS: an algebraic equation
 - Pressure of mixture = f (composition, volume, temperature)
 - Through standard thermodynamic relationships, the fugacity, enthalpy, etc. for the mixture can be determined
 - These properties can be calculated for any density; therefore, both liquid and vapor properties, as well as supercritical phenomena, can be determined

$$f_i^v = \phi_i^v y_i P \quad f_i^l = \phi_i^l x_i P$$

Phase Equilibria

- Activity-coefficient models: can only be used to calculate liquid-state fugacities and enthalpies of mixing
 - $\gamma_i = f$ (composition, temperature)
 - Cannot be used for supercritical or non condensable components because it is a correction factor for ideal-solution model (Raoult's law)

$$f_i^l = \gamma_i x_i f_i^0$$

Equations of State

- Recommended for simple systems (nonpolar, small molecules) and in regions where activity-coeff. models are inappropriate.
- Default fugacity model: Soave-Redlich-Kwong (SRK) or Peng-Robinson (PR)
 - Normally use three pure-component parameters per substance and one binary-interaction parameter per binary pair
 - Give qualitatively correct results even in the supercritical region
 - Poor predictors of enthalpy changes except for light hydrocarbons and they are not quantitatively accurate for phase equilibria
 - Good for systems containing hydrocarbons and light gases

Equation of State

The simplest EOS is an ideal gas law, a combination of Boyle and Charle's law

$$Pv = RT \longrightarrow P = RT/v \quad (\text{pressure-explicit form})$$

Why pressure-explicit form?

$$\ln \hat{\phi}_i^v = -\frac{1}{RT} \int_{\infty}^{v^v} \left[\left(\frac{\partial P}{\partial n_i} \right)_{T,V,n_{j \neq i}} - \frac{RT}{V} \right] dV - \ln Z^v$$

$$\ln \hat{\phi}_i^l = -\frac{1}{RT} \int_{\infty}^{v^l} \left[\left(\frac{\partial P}{\partial n_i} \right)_{T,V,n_{j \neq i}} - \frac{RT}{V} \right] dV - \ln Z^l$$

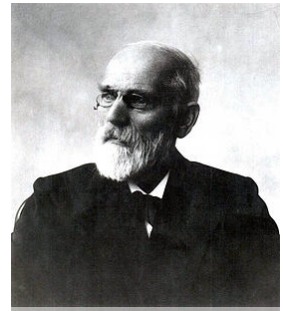
Ideal Gas Law

- Assumptions
 - 1st assumption
 - ▶ Molecules have no size
 - ▶ As T approaches zero or P approaches infinity, V equals zero
 - 2nd assumption
 - ▶ Molecules do not interact with each other
 - ▶ They never condense to liquefy

van der Waals EOS

The van der Waals theory (1873) assumes molecules have finite limiting volume b and attract one another according to a/v^2 1910 노벨상 수상

- Molecules have finite size
- 'b': Liquid molar volume (b: size parameter)
- Molecules to interact with each other
- 'a/V²': attractive pressure (a: energy parameter)



https://ko.wikipedia.org/wiki/요하너스_디데릭_판데르발스

Step 1

Real gas has finite size since it liquefies whereas ideal gas has no size when the pressure approaches infinity or temperature goes to absolute zero point

$$v^{real} = v^{ideal} + b = \frac{RT}{P} + b$$

$$P = \frac{RT}{v - b}$$

Step 2

Pressure exerted by real gas is less than $P = RT/(v-b)$ by a/v^2 due to the existence of intermolecular forces

$$P = \frac{RT}{v-b} - \underbrace{C_1 \times C_2}_{\substack{\downarrow \\ \propto \frac{n_1}{v} \times \frac{n_2}{v} = \frac{a}{v^2}}} \quad \text{공간 내 분자 밀도와 관련}$$

논문 제목: On the continuity of vapor phase into condensed liquid phase with a same tool; equation of state

증기상, 액상, 증기+액상 공존을 모두 _____으로!

Vapor Pressure of CH₃Cl at 322K with vdw EOS

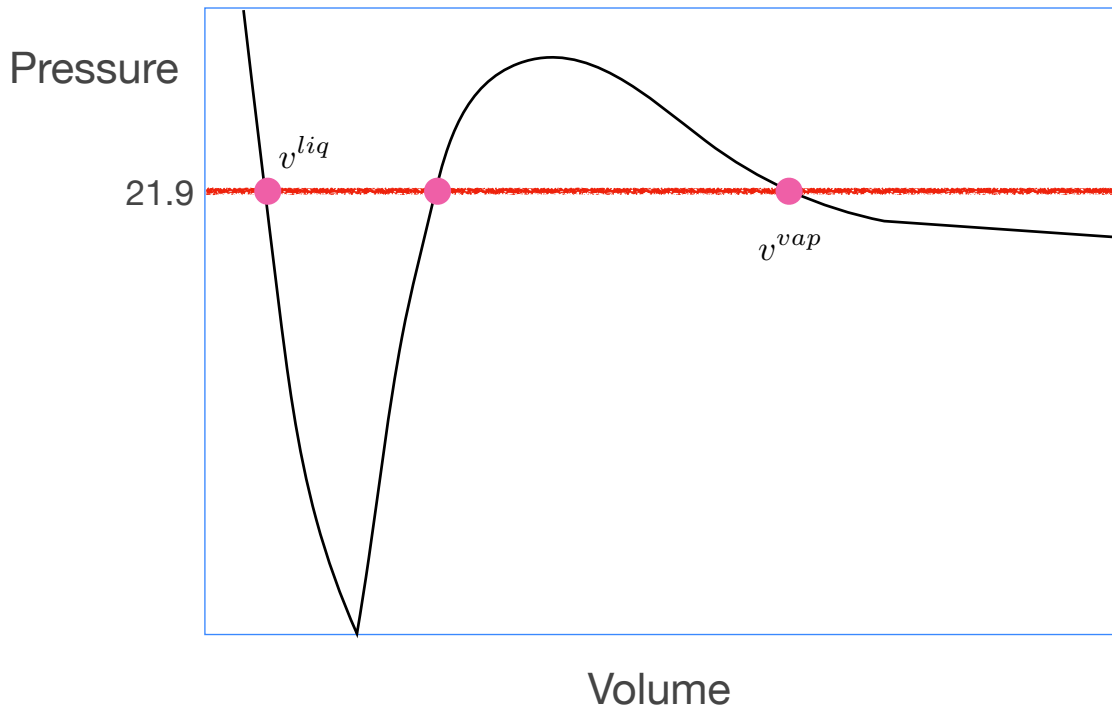
Terms	Value
T _c (K)	416.3
P _c (atm)	65.9
P _{vap} (322K)	10.49
R	0.08206
T (k)	322

$$a = \frac{27}{64} \times \frac{R^2 T_c^2}{P_c} = \frac{27}{64} \times \frac{(0.08206)^2 (416.3)^2}{65.9} = 7.4709$$

$$b = \frac{RT_c}{8P_c} = \frac{(0.08206)(416.3)}{(8)(65.9)} = 0.0648$$

$$P = \frac{RT}{v-b} - \frac{a}{v^2} = \frac{(0.08206)(322)}{v-0.0648} - \frac{7.4709}{v^2} = \frac{26.42}{v-0.0648} - \frac{7.4709}{v^2}$$

$$P^{vap} = 21.9 \text{ atm} > 10.4 \text{ atm}$$



Equations of State

Peng-Robinson EOS

$$P = \frac{RT}{V - b} - \frac{a}{V(V + b) + b(V - b)}$$

with the van der Waals mixing rules,

$$a = \sum_i \sum_j z_i z_j \sqrt{a_i a_j} (1 - k_{ij}) \quad b = \sum_i x_i b_i$$

BIP (Binary Interaction Parameters)

➡ fugacity for phase equilibrium

e.g.) @ constant T $dG = V dP$ $\ln \frac{f_2}{f_1} = \int_{p_1}^{p_2} \frac{V}{RT} dP$

There are usually six to ten EOS choices, and a few mixing-rule choices

Example 13.4 Calculate the methane vapor molar flowrate from a flash

Temperature: 225K, Pressure: 60.78 bar

Feed flowrates:

Carbon dioxide 6 kmol/h

Hydrogen sulfide 24 kmol/h

Methane 66 kmol/h

Ethane 3 kmol/h

Propane 1 kmol/h

	DB BIPs	Zero BIPs
Peng-Robinson	52.0 kmol/h	32.5 kmol/h
SRK	60.1 kmol/h	50.5 kmol/h

Liquid-State Activity-Coefficient Models

If the conditions are far from the critical region of the mixture or that of the major component, and if experimental data are available for the VLE or LLE, a liquid-state activity-coefficient model is a reasonable choice

$$\hat{\phi}_i^v y_i P = P_i^* x_i \gamma_i \phi_i^* \exp \left(\frac{1}{RT} \int_{P_i^*}^P v_i^l dP \right) \quad \gamma_i = \frac{\hat{a}_i}{x_i} \neq 1$$

The most frequently-used activity coefficient models are the Wilson, NRTL, and UNIQUAC

Liquid-State Activity-Coefficient Models



Towler and Sinnott, 2nd Ed.

Model	Features
Wilson Equation	Uses 2 adjustable parameters to model binary interactions between molecules. Can be extended to multicomponent systems using only binary parameters. Cannot predict formation of a second liquid phase.
NRTL (Non-Random Two-Liquid) Equation	Uses 3 parameters for each binary pair, where two are energies of interaction and the third is a randomness factor. Can predict liquid-liquid or vapor-liquid equilibrium.
UNIQUAC (Universal Quasi-Chemical) Equation	Mathematically more complex than NRTL, but uses fewer adjustable parameters. Can predict liquid-liquid and vapor-liquid equilibrium. In the absence of experimental data, the parameters can be predicted by the UNIFAC method. Probably most widely-used model (?)

Others



Towler and Sinnott, 2nd Ed.

- Sour-water Systems
 - Water containing carbon dioxide, hydrogen sulfide, and ammonia. Special correlations have been developed to handle the VLE of such systems, and these are incorporated in most simulators.
- Electrolyte Systems
 - When water and salts are present in a mixture then the salts can dissociate into ions in aqueous solution. The phase-equilibrium model must account for dissociation and the presence of long-range interactions between charges on ions as well as VLE or LLE. Special electrolyte models and databases such as the OLI model have been developed. These models are available in the commercial simulators, but with additional fee.