
General Thermodynamics for Process Simulation

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Four Criteria for Equilibria

| Situation | Condition |
|--|-----------------------------|
| $T^\alpha = T^\beta$ | Thermal Equilibrium |
| $P^\alpha = P^\beta$ | Mechanical Equilibrium |
| $\mu_i^v = \mu_i^l, \mu_i^{l1} = \mu_i^{l2}$ | Phase Equilibria (VLE, LLE) |
| $\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = 0$ | Chemical Equilibrium |

Fugacity (or chemical potential) is defined as an **escaping tendency** of a component 'i' in a certain phase into another phase.



Basic Phase Equilibria Relations

➤ Vapor-liquid equilibrium calculations

The basic relationship for every component in vapor-liquid equilibrium is:

$$\hat{f}_i^v(T, P, y_i) = \hat{f}_i^l(T, P, x_i) \quad (1)$$

where

\hat{f}_i^v : the fugacity of component i in the vapor phase

\hat{f}_i^l : the fugacity of component i in the liquid phase



Basic Phase Equilibria Relations

↗ There are two methods for representing liquid fugacities.

- Equation of state method
- Liquid activity coefficient method



Equation of State Method

➤ The equation of state method defines fugacities as:

$$\hat{f}_i^v = \hat{\phi}_i^v y_i P \quad (2)$$

$$\hat{f}_i^l = \hat{\phi}_i^l x_i P \quad (3)$$

where:

ϕ_i^v is the vapor phase fugacity coefficient
 ϕ_i^l is the liquid phase fugacity coefficient
 y_i is the mole fraction of i in the vapor
 x_i is the mole fraction of i in the liquid
 P is the system pressure



Equation of State Method

➤ We can then rewrite equation 1 as:

$$\hat{\phi}_i^v y_i = \hat{\phi}_i^l x_i \quad (4)$$

➤ This is the standard equation used to represent vapor-liquid equilibrium using the equation-of-state method.

➤ ϕ_i^v and ϕ_i^l are both calculated by the equation-of-state.

➤ Note that K-values are defined as:

$$K_i = \frac{y_i}{x_i} \quad (5)$$



Liquid Activity Coefficient Method (VLE)

The activity coefficient method defines liquid fugacities as:

$$\hat{f}_i^l = \gamma_i x_i f_i^0 \quad (6)$$

The vapor fugacity is the same as the EOS approach:

$$\hat{f}_i^v = \hat{\phi}_i^v y_i P \quad (7)$$

where:

γ_i is the liquid activity coefficient of component i

f_i^0 is the standard liquid fugacity of component i

$\hat{\phi}_i^v$ is calculated from an equation-of-state model

We can then rewrite equation 1 as:

$$\hat{\phi}_i^v y_i P = x_i \gamma_i f_i^0 \quad (8)$$



Liquid Activity Coefficient Method (LLE)

- For Liquid-Liquid Equilibrium (LLE) the relationship is:

$$\hat{f}_i^{l1} = \hat{f}_i^{l2} \quad (9)$$

where the designators 1 and 2 represent the two separate liquid phases.

- Using the activity coefficient definition of fugacity, this can be rewritten and simplified as:

$$x_i^{l1} \gamma_i^{l1} = x_i^{l2} \gamma_i^{l2} \quad (10)$$



K-values

↗ The k-values can be calculated from:

$$K_i = \frac{y_i}{x_i} = \frac{\gamma_i^l \phi_i^{sat} P_i^{sat} \exp\left[\frac{V_i^l}{RT} (P - P_i^{sat})\right]}{\hat{\phi}_i^v P} \quad (11)$$

Or

$$K_i = \frac{y_i}{x_i} = \frac{\hat{\phi}_i^l}{\hat{\phi}_i^v} \quad (12)$$



Example 2: Ideal Raoult's Law

The preceding equation reduces to the following ideal Raoult's law:

$$y_i P = x_i P_i^{vap}$$

Example : Pxy plot at constant T(75°C). (P in kPa, T in °C)

$$\ln P_1^{vap} = 14.2724 - \frac{2945.47}{t + 224}, \quad \ln P_2^{vap} = 14.2043 - \frac{2972.64}{t + 209}$$

Solution

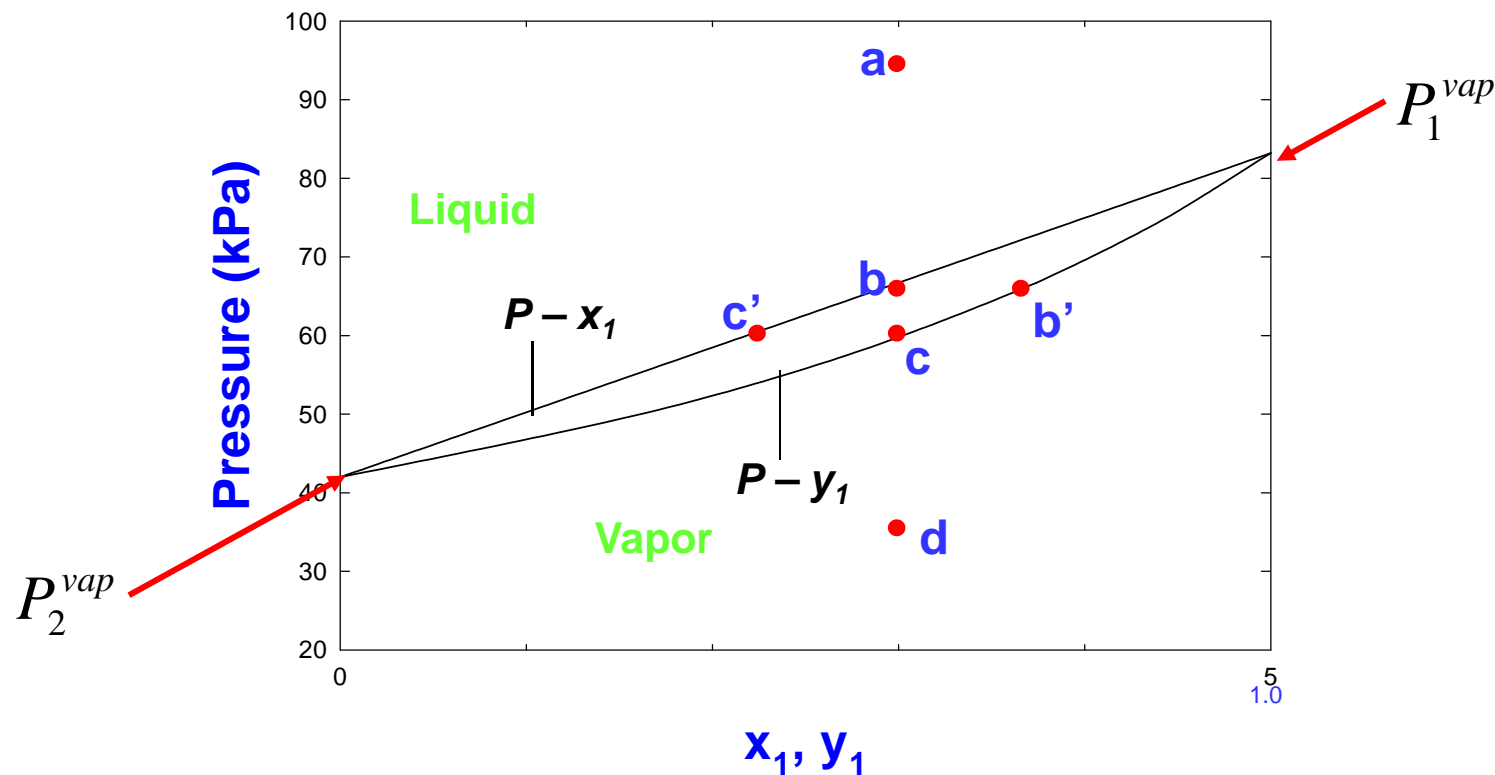
At 75°C, $P_1^{vap} = 83.21 \text{ kPa}$ and $P_2^{vap} = 41.98 \text{ kPa}$

The total pressure $P = x_1 P_1^{vap} + x_2 P_2^{vap}$, $P = P_2^{vap} + (P_1^{vap} - P_2^{vap})x_1$

Vapor phase composition, $y_1 = \frac{x_1 P_1^{vap}}{P_2^{vap} + (P_1^{vap} - P_2^{vap})x_1} = \frac{x_1 P_1^{vap}}{P}$



Pxy Diagram at Constant Temperature



Example 3: Slightly Non-ideal System

For systems which the liquid phase behaves nonideally:

$$y_i P = \gamma_i x_i P_i^{vap}$$

Relation between activity coefficient and excess Gibbs energy is as:

$$\ln \gamma_i = \left[\frac{\partial (nG^{ex} / RT)}{\partial n_i} \right]_{T,P,n_{j \neq i}}$$

As an example, excess Gibbs energy expression is as:

$$\frac{G^{ex}}{RT} = Ax_1 x_2$$

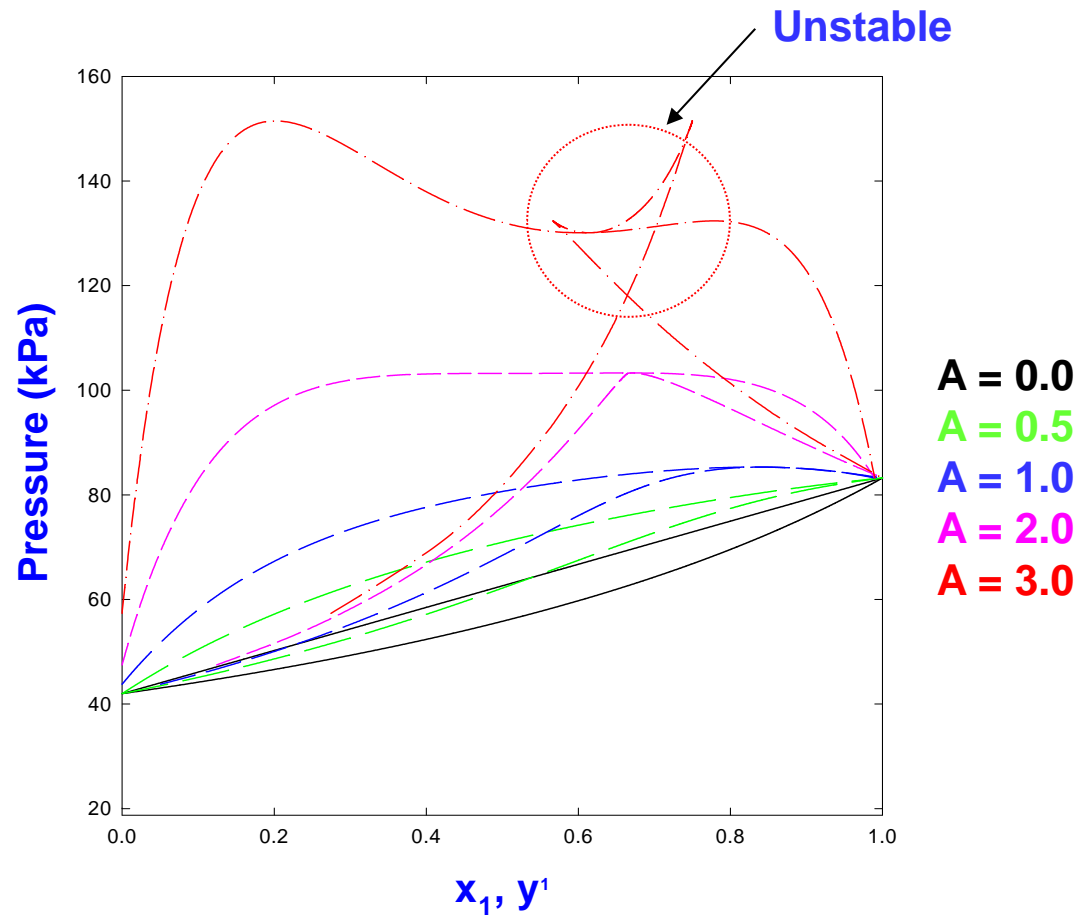
Therefore, γ_1 and γ_2 becomes.

$$\gamma_1 = \exp(Ax_2^2) \quad \gamma_2 = \exp(Ax_1^2)$$

So, $P = \exp[A(1-x_1)^2] x_1 P_1^{vap} + \exp(Ax_1^2) x_2 P_2^{vap}$ $y_1 = \frac{\exp[A(1-x_1)^2] x_1 P_1^{vap}}{P}$



Prediction with Margules Equations

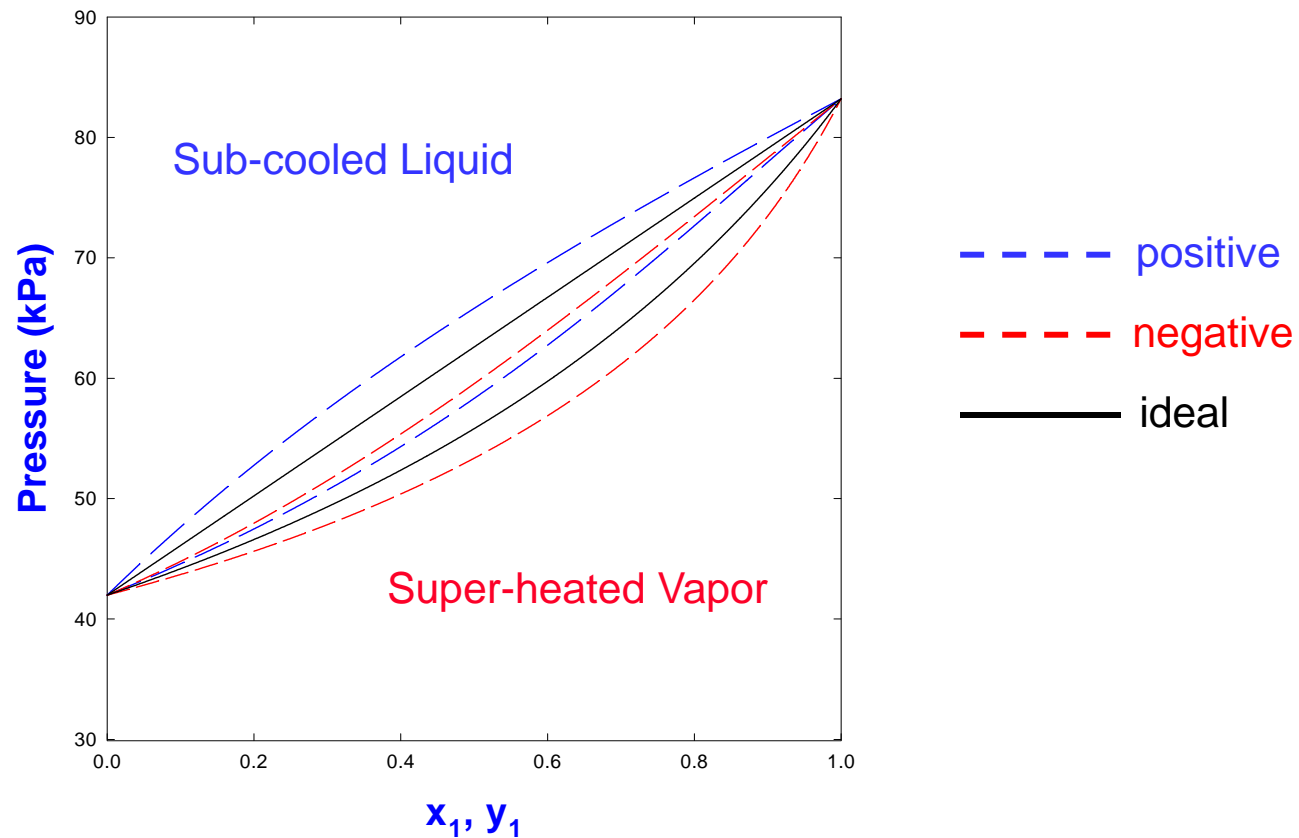


Deviations from Raoult's Law (1 of 2)

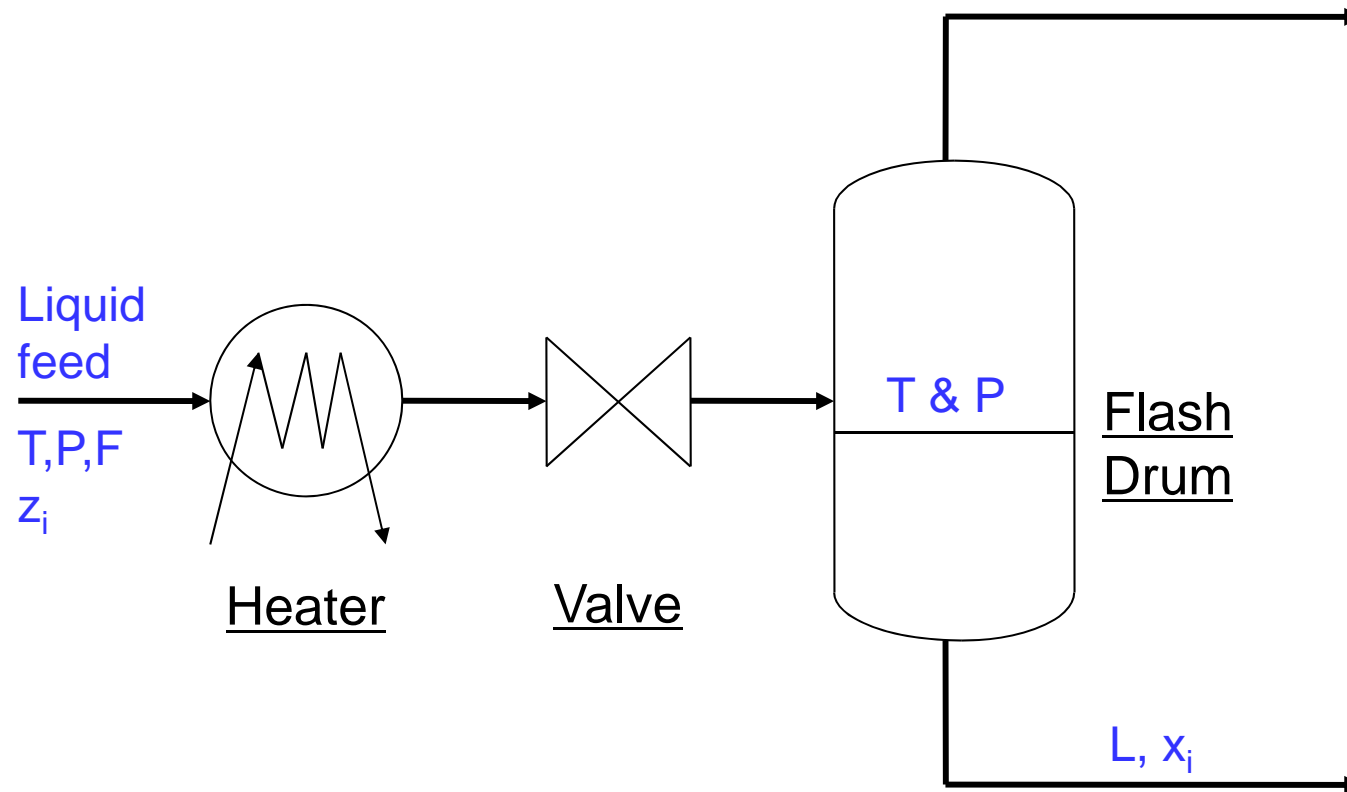
- In general, you can expect non-ideality of unlike molecules. Either the size and shape or the intermolecular interactions between components may be dissimilar. For short, these are called size and energy asymmetry. Energy asymmetry occurs between polar and non-polar molecules and also between different polar molecules.
- In the majority of mixtures, activity coefficients is greater than unity. The result is a higher fugacity than ideal. The fugacity can be interpreted as the tendency to vaporize. If compounds vaporize more than in an ideal solution, then they increase their average distance. So activity coefficients is greater than unity indicate repulsion between unlike molecules. If the repulsion is strong, liquid-liquid separation occurs. This is another mechanism that decreases close contact between unlike molecules.
- If the activity coefficient is larger than unity, the system is said to show positive deviations from Raoult's law. Negative deviations from Raoult's law occur when the activity coefficient is smaller than unity.



Deviations from Raoult's Law (2 of 2)



Isothermal Flash Calculations



Equilibrium Flash Vaporization

- The equilibrium flash separator is the simplest equilibrium-stage process with which the designer must deal. Despite the fact that only one stage is involved, the calculation of the compositions and the relative amount of the vapor and liquid phases at any given pressure and temperature usually involves a tedious trial-and-error solution.

Buford D. Smith, 1963



Flash Calculation (1 of 4)

- MESH Equation
- Material Balance
- Equilibrium Relations
- Summation of Compositions
- Enthalpy(H) Balance



Flash Calculation (2 of 4)

➤ Overall Material Balance

$$F = V + L \quad (1)$$

➤ Component Material Balance

$$Fz_i = Vy_i + Lx_i \quad (2)$$

➤ Equilibrium Relations

$$y_i = K_i x_i \quad (3)$$



Flash Calculation (3 of 4)

➤ Summation of Compositions

$$\sum_i x_i = 1 \quad (4a)$$

$$\sum_i y_i = 1 \quad (4b)$$

➤ Defining

$$\phi = V / F \quad (5)$$

➤ Combining (1) through (5), we obtain:

$$F(\phi) = \sum_i \frac{z_i(1 - K_i)}{1 + \phi(K_i - 1)} = 0 \quad (6)$$



Flash Calculation (4 of 4)

➤ From ideal Raoult's law

$$y_i P = x_i P_i^{vap} \quad (7)$$

➤ K-value can be rewritten as:

$$K_i = \frac{y_i}{x_i} = \frac{P_i^{vap}}{P} \quad (8)$$

➤ From Antoine equation

$$\log P_i^{vap} (kPa) = A - \frac{B}{t(^{\circ}C) + C} \quad (9)$$



Antoine Coefficients

$$\log P_i^{vap} (kPa) = A - \frac{B}{t(^{\circ}C) + C}$$

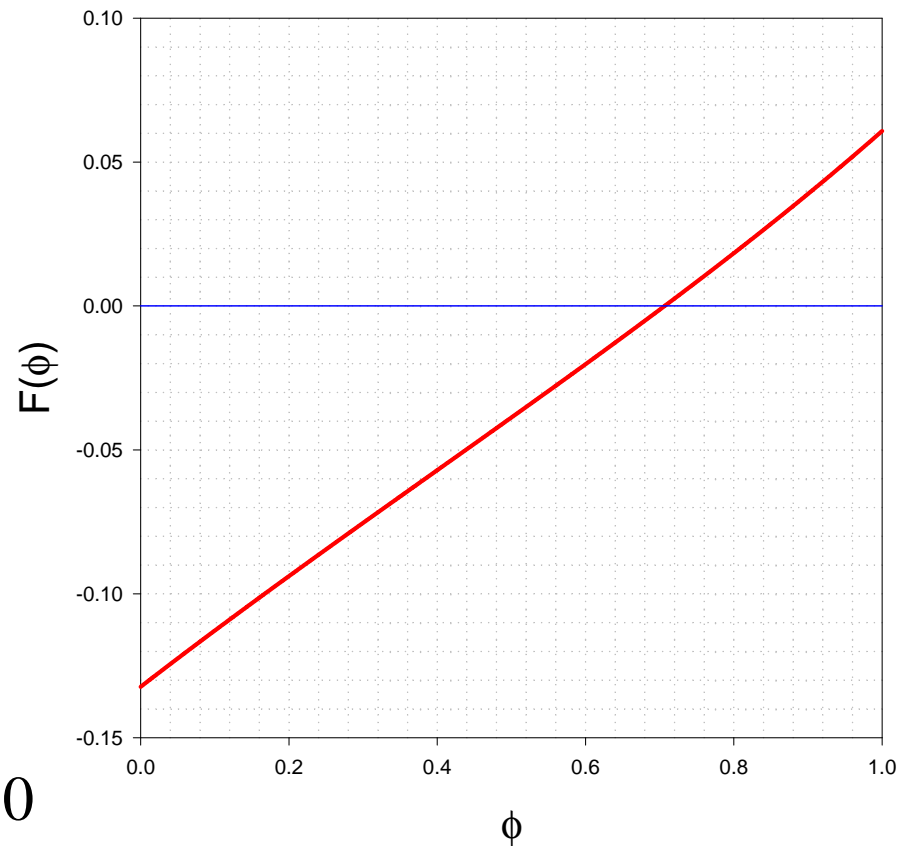
| | Benzene | Toluene |
|---|----------|----------|
| A | 6.01788 | 6.08436 |
| B | 1203.677 | 1347.620 |
| C | 219.904 | 219.787 |



Rachford-Rice Function

$$\underline{\phi = 0.707}$$

$$F(\phi) = \sum_i \frac{z_i(1-K_i)}{1+\phi(K_i-1)} = 0$$



Flash Calculation Results (1 of 3)

➤ Vapor Flowrate (K-mole/hr)

$$V = F\phi = (100) \times (0.707) = 70.7 \quad (1)$$

➤ Liquid Flowrate (K-mole/hr)

$$L = F - V = 100 - 70.7 = 29.3 \quad (2)$$



Flash Calculation Results (2 of 3)

➤ Mole Fraction at the liquid phase

$$x_i = \frac{z_i}{1 + \phi(K_i - 1)} \quad (3)$$

$$x_B = 0.4479 \quad x_T = 0.5521 \quad (4)$$

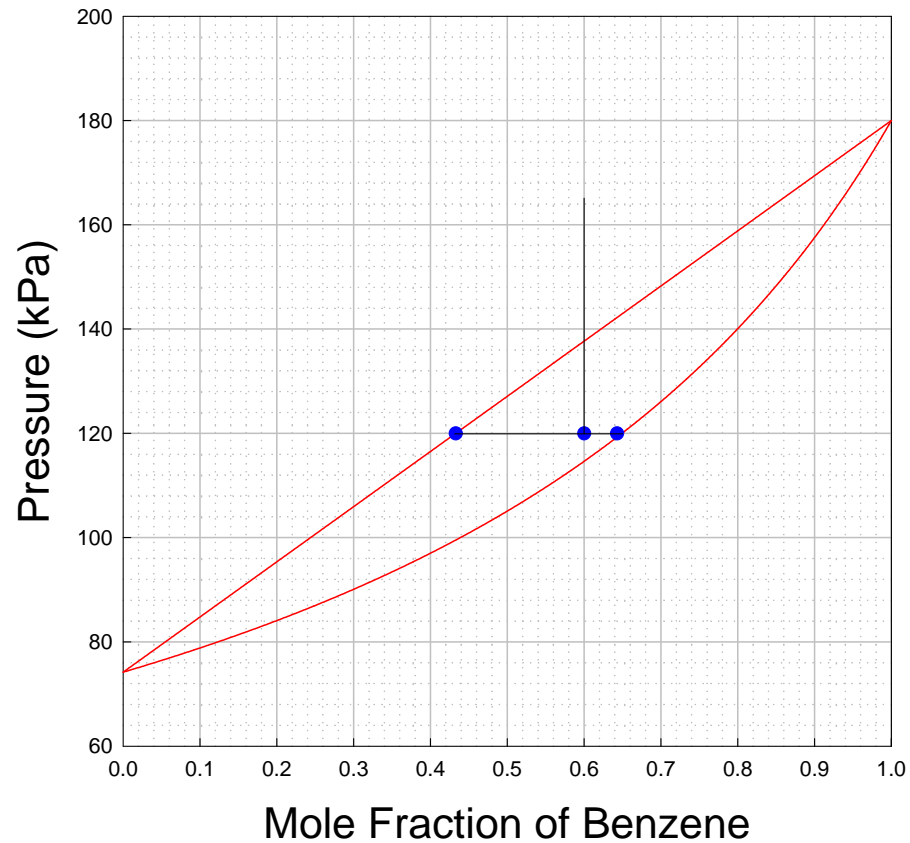
➤ Mole Fraction at the vapor phase

$$y_i = K_i x_i = \frac{K_i z_i}{1 + \phi(K_i - 1)} \quad (5)$$

$$y_B = 0.6631 \quad y_T = 0.3369 \quad (6)$$



Flash Calculation Results (3 of 3)



$$x_B = 0.4329$$

$$y_B = 0.6429$$



PRO/II Keyword Input for Flash Calculation

```
TITLE PROBLEM=PRBLEM-1A, PROJECT=CLASS, USER=JHCHO
DIMENSION METRIC, PRES=ATM
PRINT INPUT=ALL, PERC=M, FRAC=M
COMPONENT DATA
LIBID 1, BENZENE/2, TOLUENE
THERMODYNAMIC DATA
METHOD SYSTEM=IDEAL
STREAM DATA
PROP STREAM=1, TEMP=25, PRES=1, RATE=100, COMP=1, 60/2, 40
UNIT OPERATION DATA
FLASH UID=F01
FEED 1
PROD V=1V, L=1L
ISO TEMP=100, PRES=1.2
END
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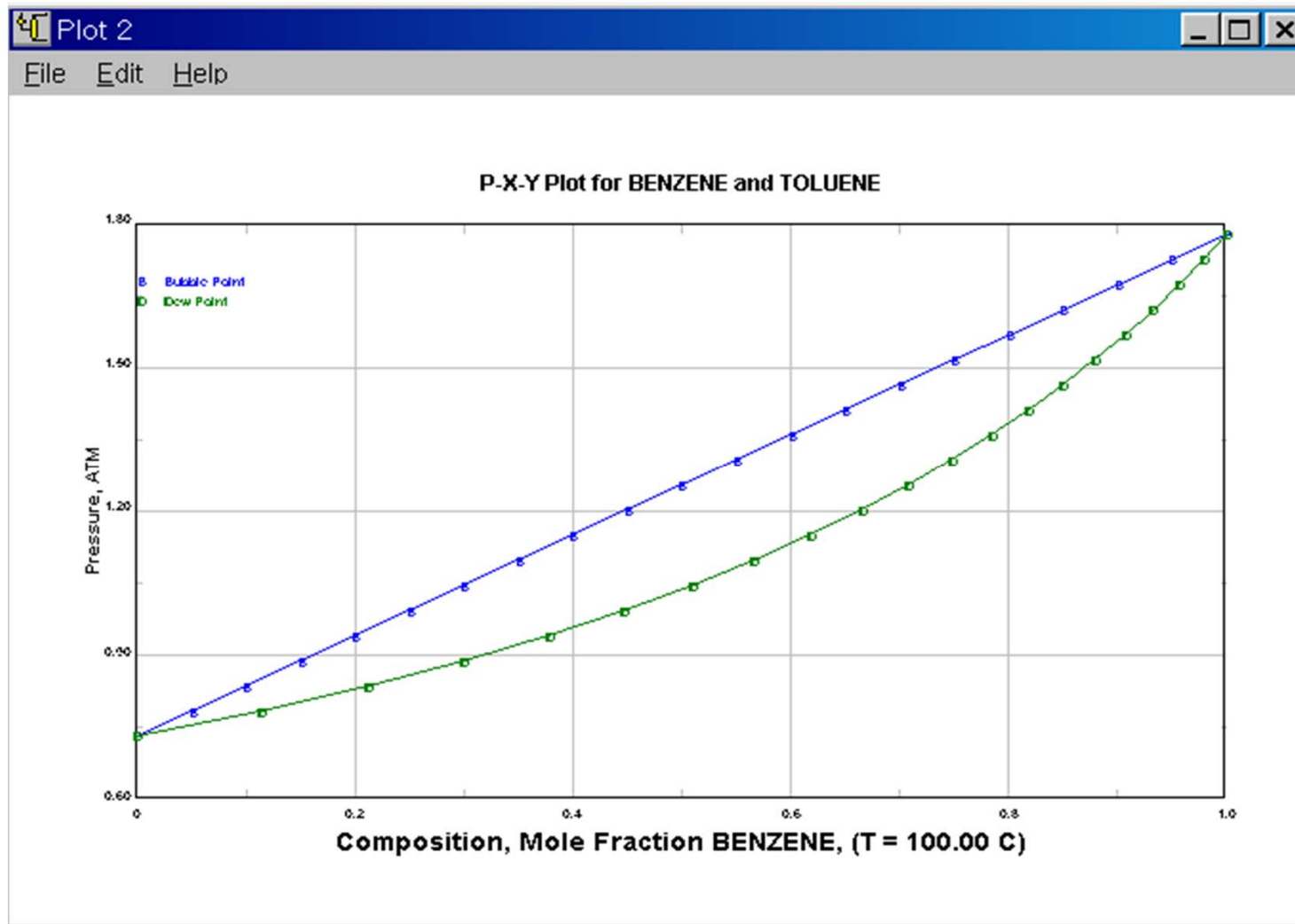


PRO/II Output Summary for Flash Calculation

| STREAM ID | 1 | 1L | 1V |
|-----------------------|----------|----------------|----------------|
| NAME | | | |
| PHASE | LIQUID | LIQUID | VAPOR |
| FLUID MOLAR FRACTIONS | | | |
| 1 BENZENE | 0.6000 | 0.4476 | 0.6629 |
| 2 TOLUENE | 0.4000 | 0.5524 | 0.3371 |
| TOTAL RATE, KG-MOL/HR | 100.0000 | 75.6710 | 24.3290 |
| TEMPERATURE, C | 25.0000 | 100.0000 | 100.0000 |
| PRESSURE, ATM | 1.0000 | 1.2000 | 1.2000 |
| ENTHALPY, M*KCAL/HR | 0.0865 | 0.2800 | 0.2681 |
| MOLECULAR WEIGHT | 85.1285 | 85.8632 | 82.8433 |
| MOLE FRAC VAPOR | 0.0000 | 0.0000 | 1.0000 |
| MOLE FRAC LIQUID | 1.0000 | 1.0000 | 0.0000 |



PRO/II BVLE Analysis



Thermodynamic Models built in Simulator



Dew & Bubble Point Calculation

➤ **Dew Point** is the very state at which condensation is about to occur.

- Dew Point Temperature Calculation at a Given Pressure
- Dew Point Pressure Calculation at a Given Temperature
- Vapor Fraction is '1' at Dew Point

➤ **Bubble Point** is the very state at which vaporization is about to occur.

- Bubble Point Temperature Calculation at a Given Pressure
- Bubble Point Pressure Calculation at a Given Temperature
- Vapor Fraction is '0' at Bubble Point



Ex-1: Bubble Point Failure Case

- Calculate the bubble point pressure at 85°C of the following stream. Did you get a converged solution? If not, why?
- Use SRK for your simulation.

| Component | Mole % |
|-----------|--------|
| C1 | 65 |
| C2 | 15 |
| C3 | 15 |
| IC4 | 5 |

Save as Filename:
EX-1.inp



Difference between Gas and Vapor

- ↗ For gas, $T > T_c$
- ↗ For vapor, $T < T_c$
- ↗ T: System temperature, T_c : Critical temperature

- ↗ “Methane Gas” but not “Methane Vapor”
- ↗ “Water Vapor” but not “Water Gas”



Ex-2: C7 Plus Heavy Cut Characterization

- Calculate the bubble pressure at 45°C and dew temperature at 1.5bar of the following stream. Regard C6+ as NC6(1), NC7(2) and NC8(3) and compare the results. Use SRK for your simulation.

| Component | Mole % |
|-----------|--------|
| C1 | 5 |
| C2 | 10 |
| C3 | 15 |
| IC4 | 10 |
| NC4 | 20 |
| IC5 | 15 |
| NC5 | 20 |
| C6+ | 5 |

Save as Filename:
EX-2A.inp for NC6,
EX-2B.inp for NC7,
EX-2C.inp for NC8



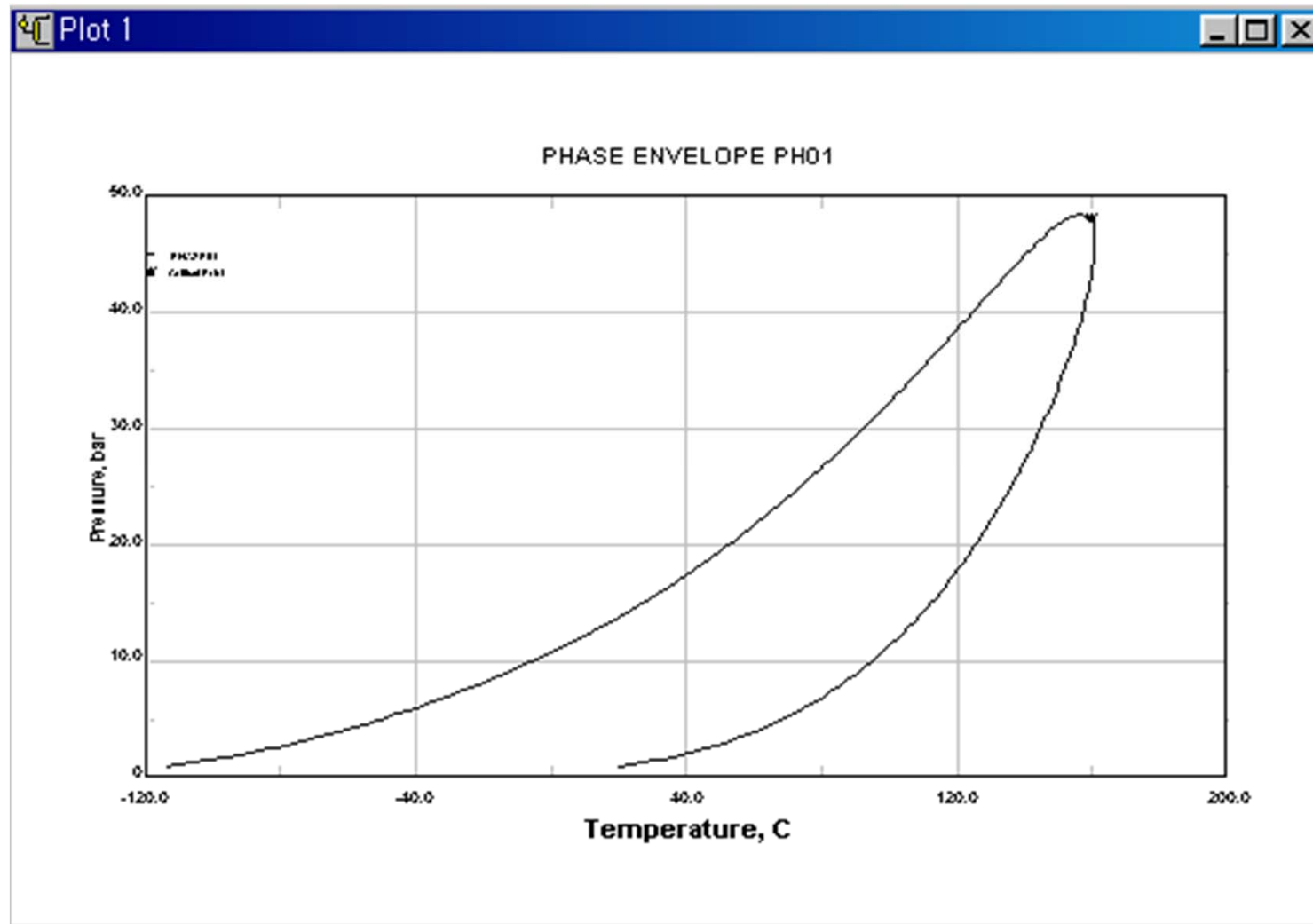
Results for EX-2

- Characterization of heavycut is very important in the calculation of dew point temperature.
- EX-2A.inp, EX-2B.inp, EX-2C.inp

| Bubble P at 45°C | Dew T at 1.5bar | C6 Plus |
|---------------------|--------------------|---------|
| 18.505 | 30.519 | NC6 |
| 18.561 | 42.783 | NC7 |
| 18.669 | 59.585 | NC8 |



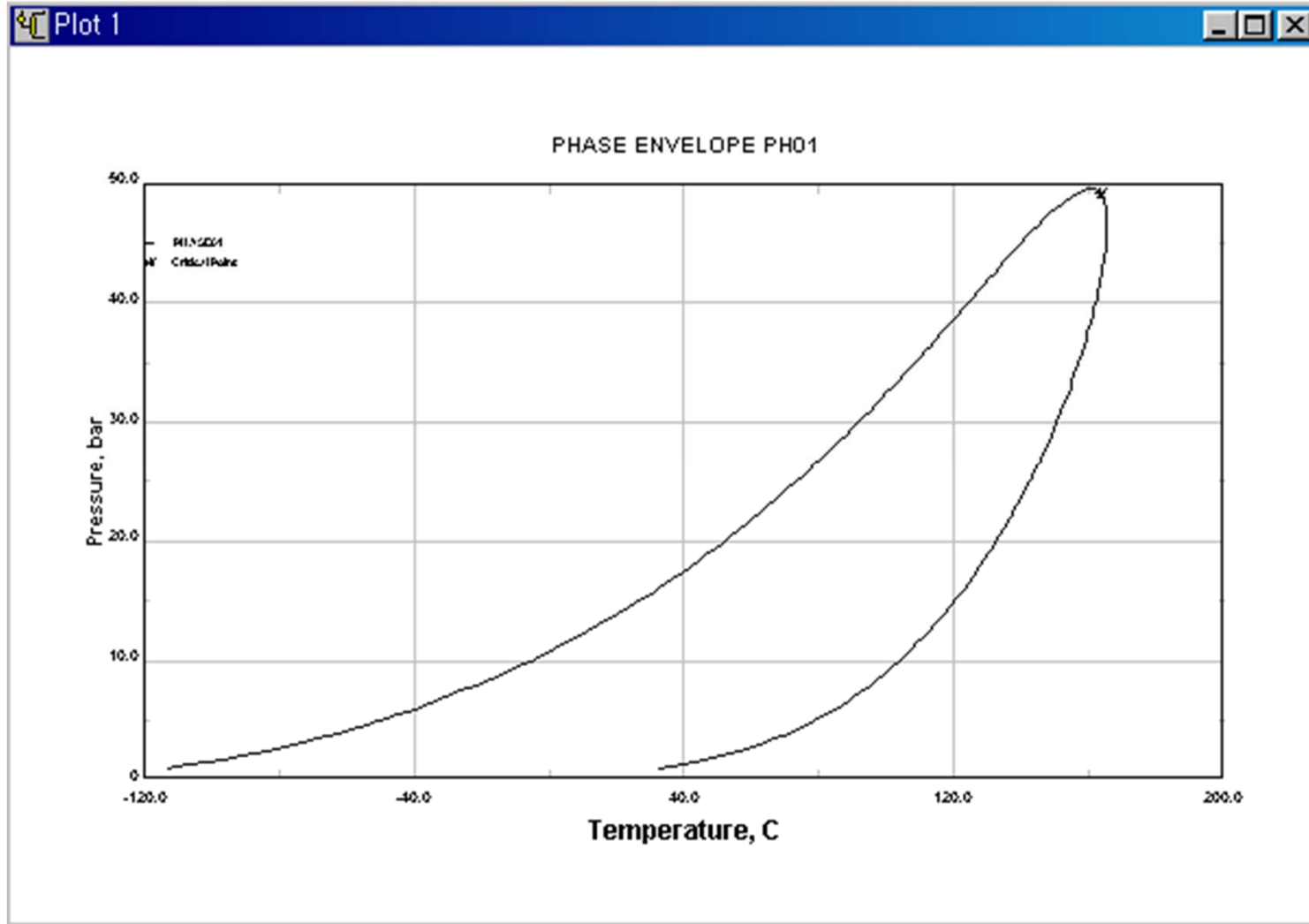
Results for EX-2A (C6+ → NC6)



Thermodynamic Models built in Simulator



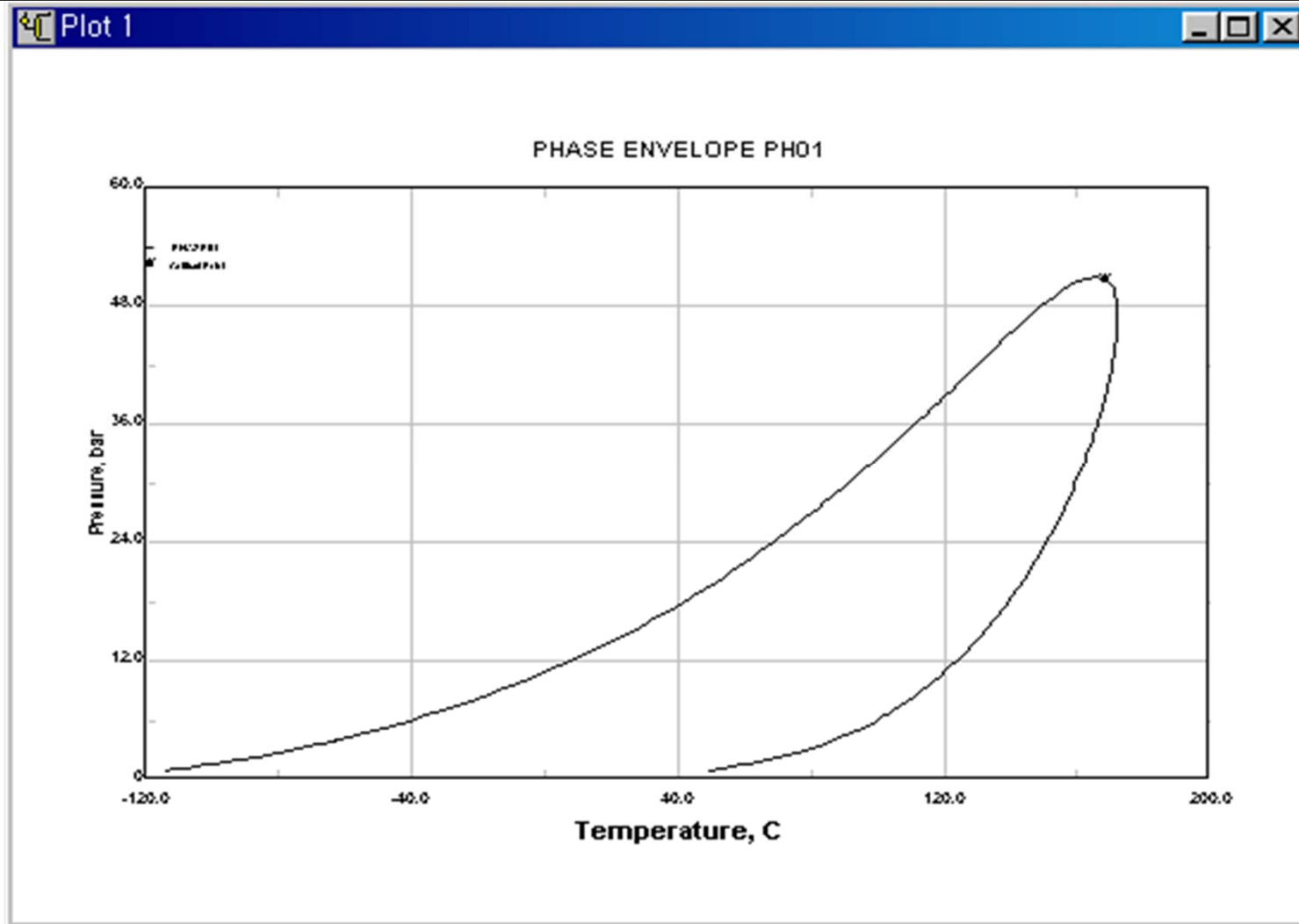
Results for EX-2B (C6+ → NC7)



Thermodynamic Models built in Simulator



Results for EX-2C (C6+ → NC8)



Thermodynamic Models built in Simulator



The End of General Thermodynamics

The End....

