

Phase equilibrium: Vapor/Liquid Equilibrium

CHE F213

CHEMICAL ENGINEERING THERMODYNAMICS

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Why study phase equilibrium?

- ❑ Most chemical engineering operations involve transfer of mass from one phase to another at different pressures and temperatures
- ❑ Understanding of these systems is important from designing and analysis view point
- ❑ Knowledge of phase equilibrium data is required for quantitative treatment of mass transfer (distillation) and chemical reactions (reaction equilibrium)
- ❑ The most commonly encountered coexisting phases in industrial practice are vapor and liquid, although liquid/liquid, vapor/solid, and liquid/solid systems are also found

Our focus will be on vapor / liquid equilibrium

The nature of equilibrium

- A static condition in which no changes occur in the **macroscopic** properties of a system with time.
- At the **microscopic** level, conditions are not static.
 - The average rate of passage of molecules is the same in both directions, and no net inter-phase transfer of material occurs.
- An isolated system consisting of liquid and vapor phases in intimate contact eventually reaches a final state wherein no tendency exists for change to occur within the system.
 - **Fixed temperature, pressure, and phase composition**

Phase rule for non-reacting system

Gibbs Phase rule: The minimum number of independent intensive variables that need to be fixed to define the state of a system

$$F = 2 - \pi + N$$

where $N \rightarrow$ no. of components, $\pi \rightarrow$ no. of phases

(The number of variables that is independently fixed in a system at equilibrium) = (the number of variables that characterize the intensive state of the system) - (the number of independent equations connecting the variable):

$$F = 2 + (N - 1)(\pi) - (\pi - 1)(N) = 2 - \pi + N$$

VLE: qualitative behavior

VLE is the state of coexistence of liquid and vapor phases

For two chemical species ($N=2$):

- The maximum value of $F = 3$ ($\pi = 1$), namely, P , T , and one mole fraction.
- All equilibrium states of the system can be represented in three-dimensional P - T -composition (x, y) space.

Figure shows P - T - xy surfaces which contain the equilibrium states of saturated vapor and saturated liquid

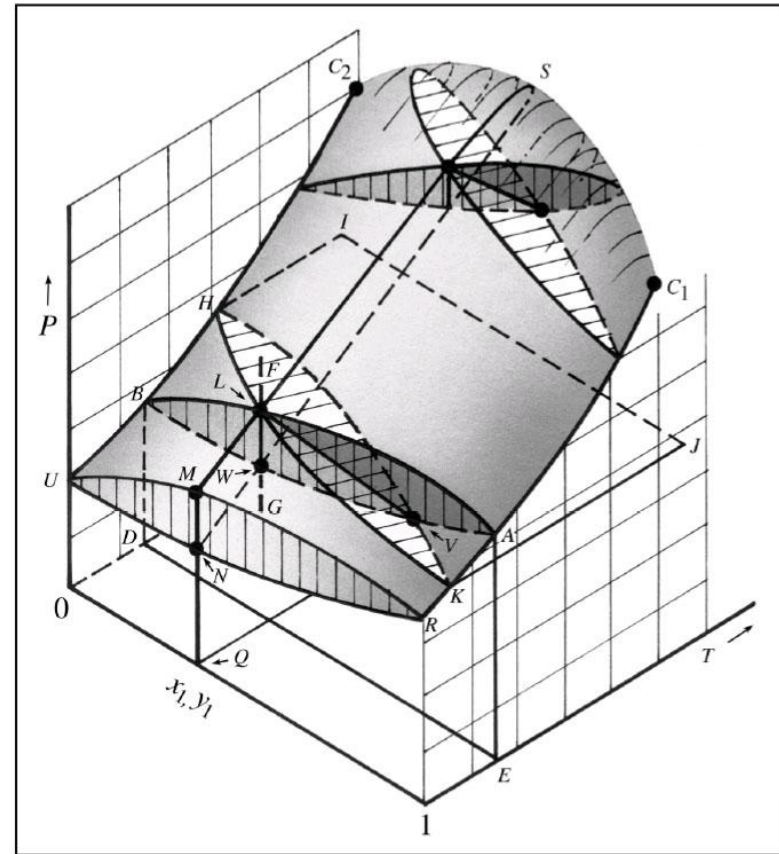
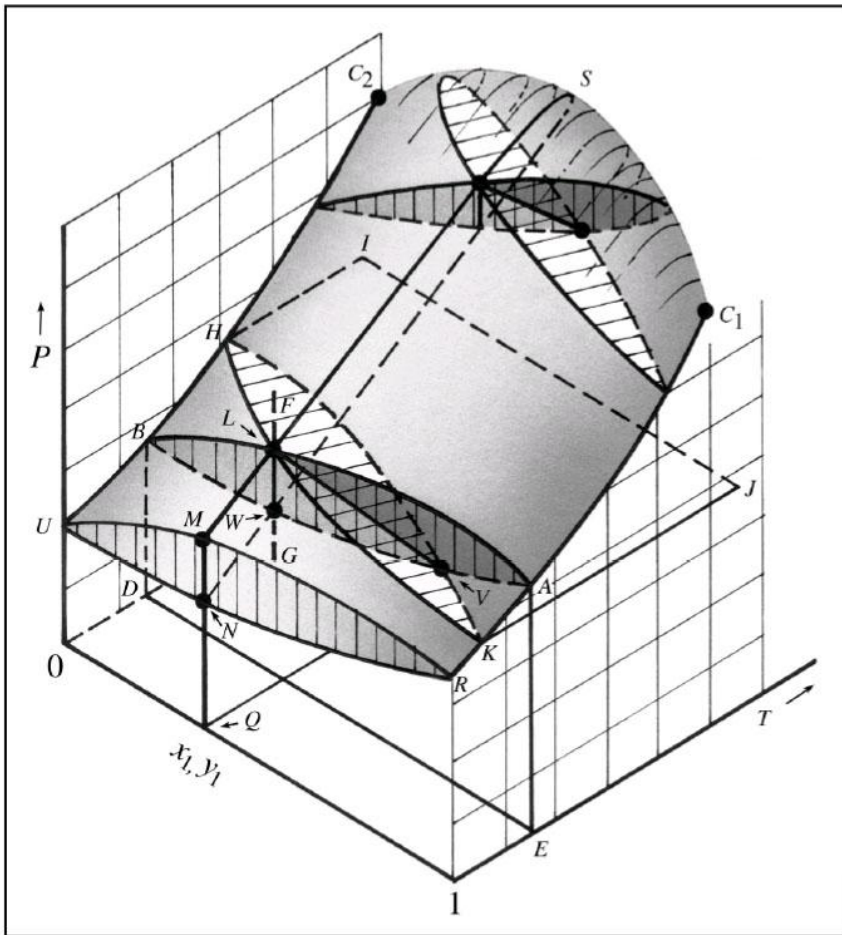


Figure 10.1: $PTxy$ diagram for vapor/liquid equilibrium.



PT-xy diagram for VLE

$x_1 \rightarrow$ liquid phase mole fraction

$y_1 \rightarrow$ vapor phase mole fraction

Here, species 1 is lighter or more volatile

- Each phase is represented by a surface
- The sub cooled-liquid region lies above the upper surface (P-T- x_1)
- The superheated-vapor region lies below the under surface (P-T- y_1)
- UBHC₂ and KAC₁ represent the vapor pressure-vs.-T curves for pure species 1 and 2
- C₁ and C₂ are the critical points of pure species 1 and 2
- The critical point of the various mixtures of two species lie along a line on the rounded edge of the surface between C₁ and C₂

- **Bubble point** : (L) The liquid just start to vaporize (first bubble of vapors appears)
- **Dew Point** : (W) The vapor just begins to condense (first drop of liquid appears)
- **Tie Line** : A line which connects points representing phases in equilibrium

P T x-y diagram for VLE

Due to complexity of three dimensional diagram, two dimensional graphs (on various plane) are generally used:

Pxy diagram at constant T [A vertical plane AEDBLA perpendicular to T axis]

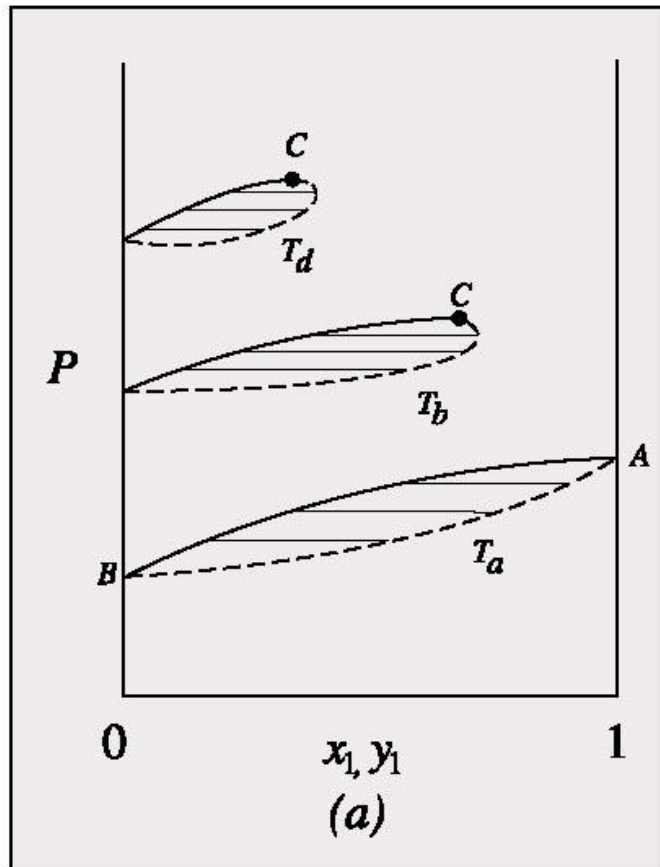
Txy diagram at constant P [A horizontal plane KJIHLK perpendicular to P axis]

PT diagram at constant composition [A vertical passes through SLMN and Q perpendicular to composition]

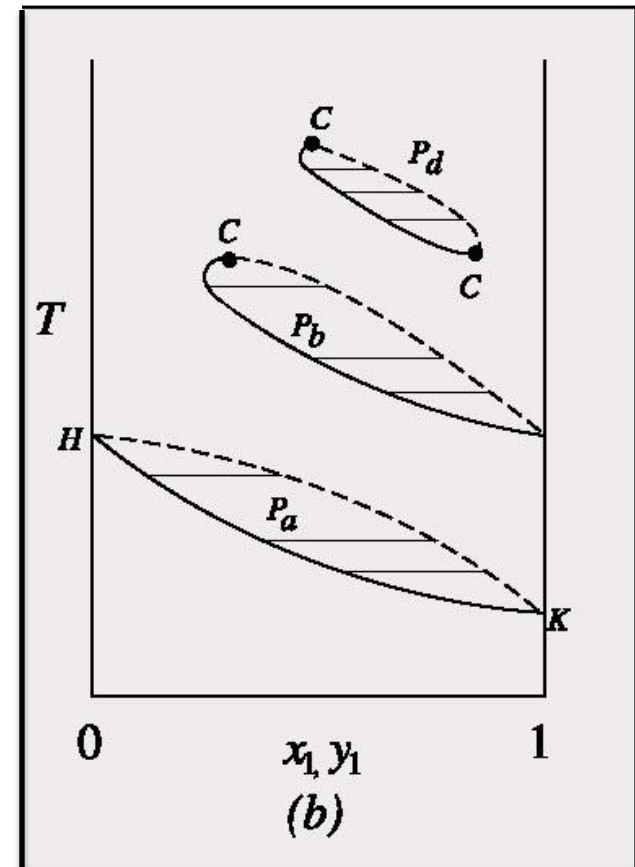
One normally plots the more volatile component

P x-y and T x-y Diagram

Figure 10.2: (a) Pxy diagram for three temperatures. (b) Txy diagram for three pressures.
— Saturated liquid (bubble line); - - - Saturated vapor (dew line)



At constant temperature



At constant pressure

Bubble point and dew point temperatures



- Any point on the saturated liquid line is the point at which the liquid just begins to boil – the first bubble of vapor is formed. This temperature, for a given composition and pressure, is the bubble-point temperature.
- Any point on the saturated vapor line is the point at which the vapor just begins to condense – the first drop of liquid is formed. This temperature, for a given composition and pressure, is the dew-point temperature.

P-T Diagram

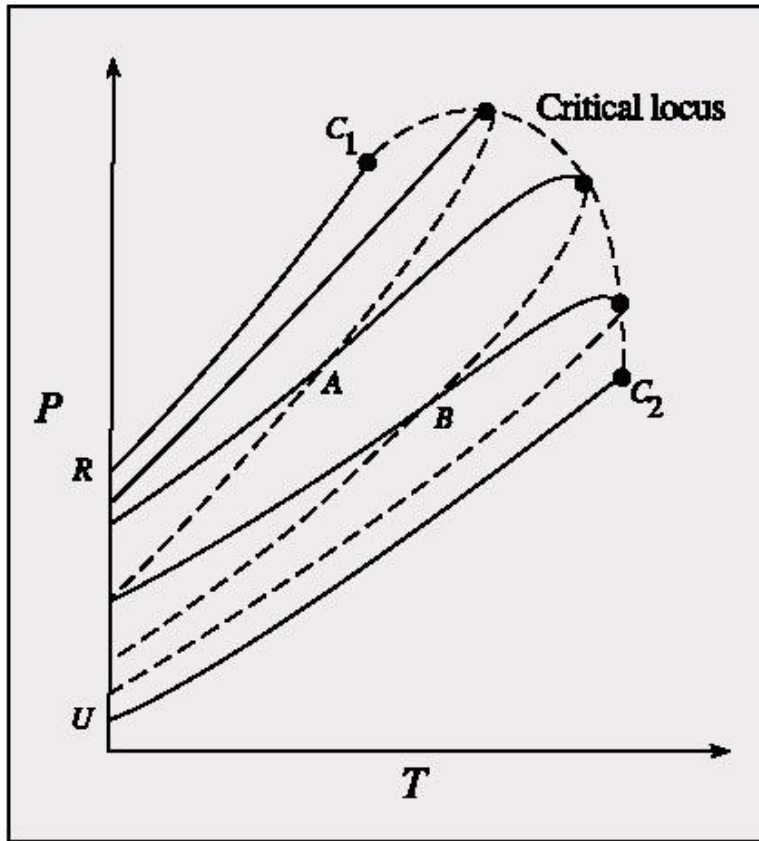


Figure 10.3: PT diagram for several compositions.

— Saturated liquid (bubble line)
- - - Saturated vapor (dew line)

- Line UC_2 and RC_1 are vapor-pressure curves for the pure species
- Each interior loop represents the P-T behavior of saturated liquid and saturated vapor for a mixture of fixed composition
- P-T relation for saturated liquid is different from that for saturated vapor of the same composition
- At point A and B in figure 10.3 saturated liquid of one composition and saturated vapor of another composition intersects (and have same T and P). The two phases are therefore in equilibrium
- The critical point for a mixture can be above that of pure substances
- Therefore under certain conditions a condensation process occurs as the result of a *reduction* in pressure

What does the T – x – y plot tell us?

- ❑ One now has two equilibrium curves – a saturated liquid line and saturated vapor line.
- ❑ Any point below the saturated liquid line is a single-phase composition of a sub-cooled liquid – no vapor exists.
- ❑ Any point above the saturated vapor line is a single-phase composition of a superheated vapor – no liquid exists.
- ❑ Any point between the saturated liquid and saturated vapor lines is a two- phase composition – both vapor and liquid exist in equilibrium.
- ❑ Thus, one can obtain a lot more information from the T vs. x,y plot than from the y vs. x

P x-y diagram for constant T

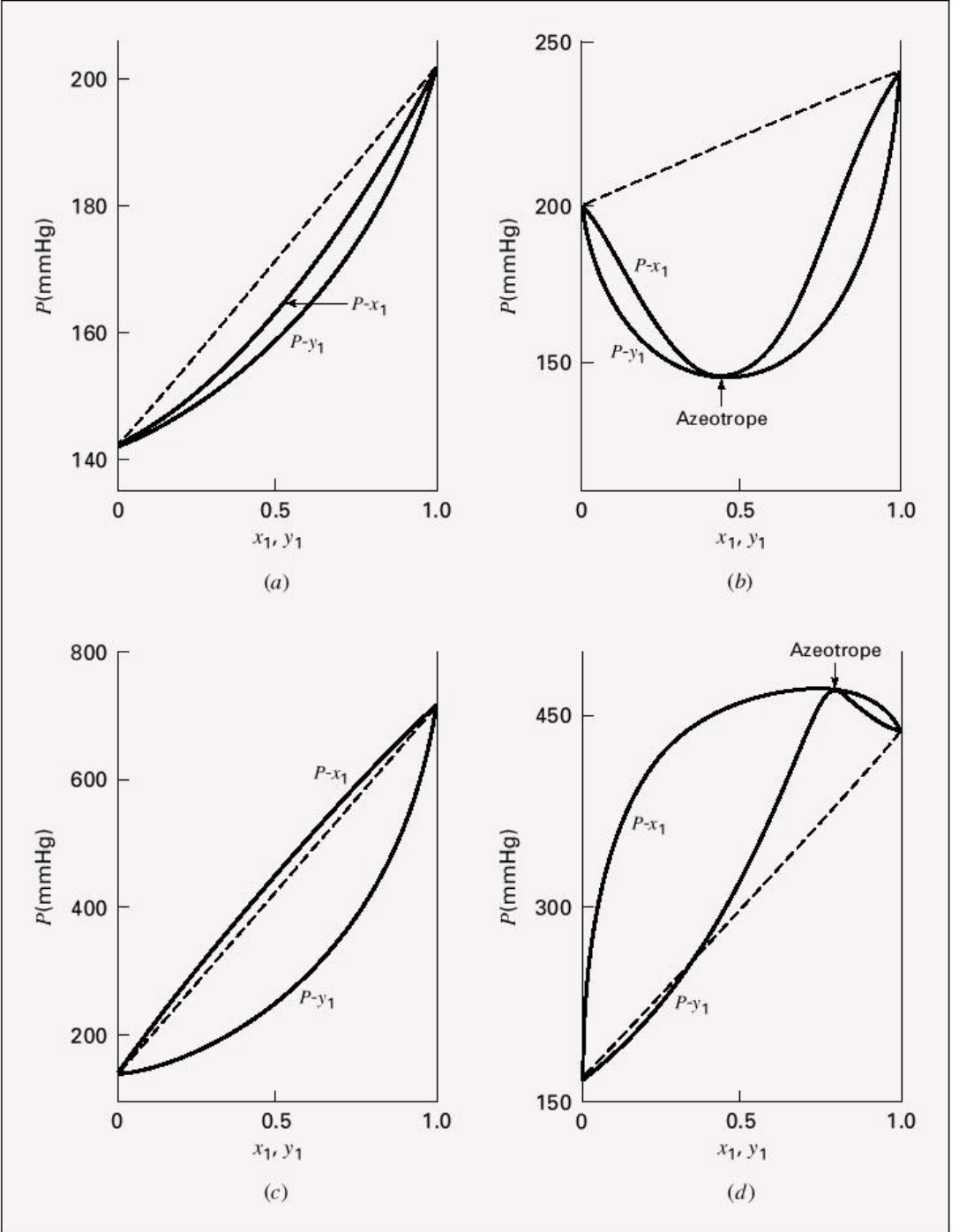
- Dashed lines shows P-x relation for Raoult's Law

(a) and (b) shows negative deviation from ideality

(c) and (d) shows positive deviation from ideality

Azeotrope: Two phases are identical in composition at this point

Such systems are not uncommon in the process industry and always pose a difficulty in purifying a mixture to compositions higher than the azeotropic point



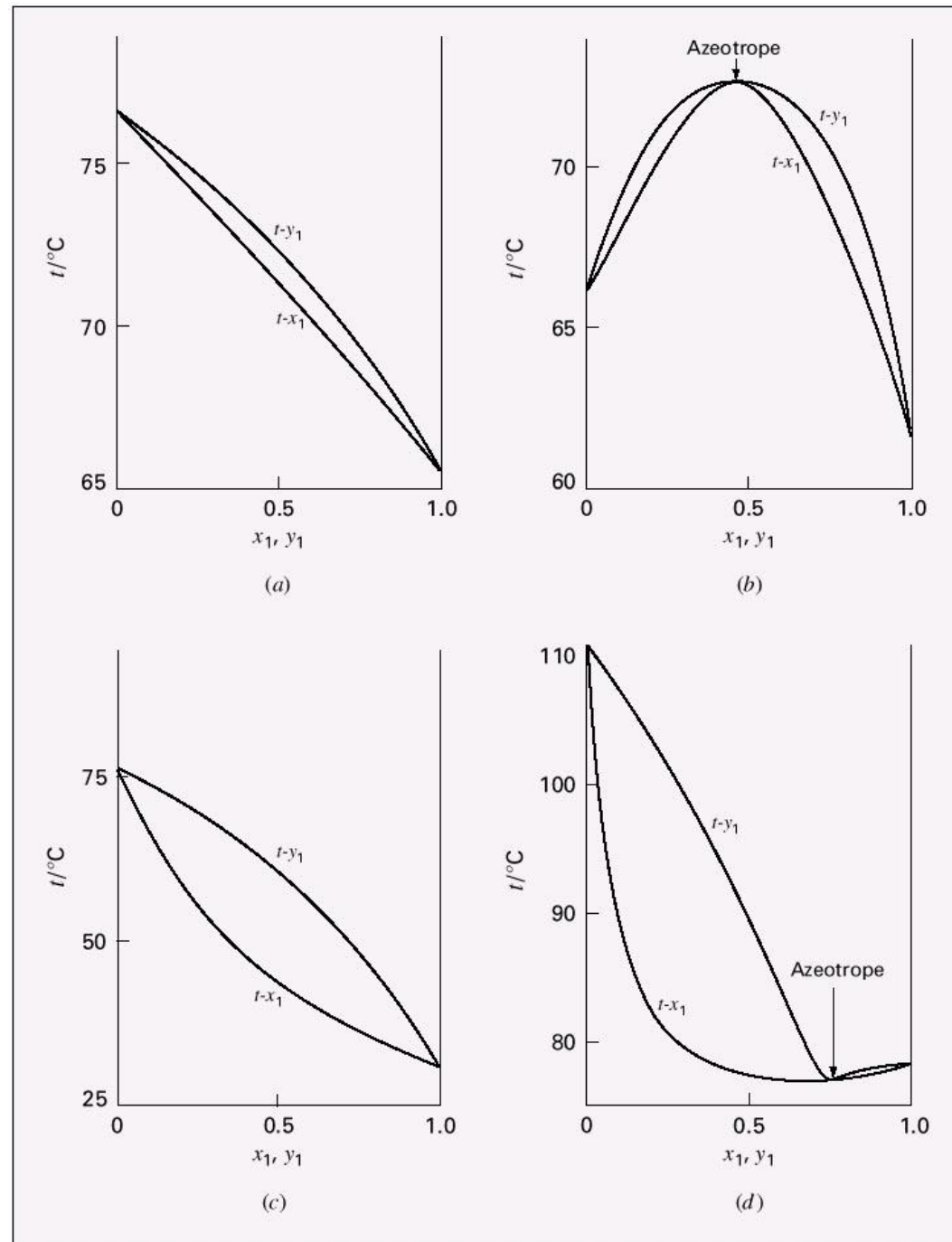
T x-y diagram for constant P

- Dashed lines shows P-x relation for Raoult's Law

(b) shows maximum boiling azeotrope

(d) shows minimum boiling azeotrope

- At azeotrope $x_i = y_i$
- The dewpoint and bubblepoint curves are tangent at this point.
- No separation at such state is possible by distillation



Simple models for VLE

Raoult's law

Assumption to apply Raoult's law

- The vapor phase is an ideal gas (apply for low to moderate pressure)
- The liquid phase is an ideal solution (apply when the species that are chemically similar)

$$y_i P = x_i P_i^{sat} \quad (i = 1, 2, \dots, N)$$

where x_i is liquid phase mole fraction, y_i is vapor phase mole fraction P_i^{sat} is vapor pressure of pure species i , and product $y_i P$ is the partial pressure of species i .

Although it provides a realistic description of actual behavior for a small class of systems, it is valid for any species present at a mole fraction approaching unity, provided that the vapor phase is an ideal gas.

A limitation of Raoult's law is that it can be applicable to species for which vapor pressure is known, and species to be 'subcritical'.

VLE Calculations

Table 7.1 Types of VLE calculations

VLE Type	Specified Variables	Computed Variables
<i>Bubble Pressure</i>	T and $\{x_i\}$	P and $\{y_i\}$
<i>Dew Pressure</i>	T and $\{y_i\}$	P and $\{x_i\}$
<i>Bubble Temperature</i>	P and $\{x_i\}$	T and $\{y_i\}$
<i>Dew Temperature</i>	P and $\{y_i\}$	T and $\{x_i\}$
<i>Flash Distillation</i>	T, P and $\{z_i\}$	L or $V, \{x_i\}$ and $\{y_i\}$

Dew and Bubble Point Calculations

Dew Point Pressure:

Given a vapor composition at a specified temperature, find the composition of the liquid in equilibrium

Given T, y_1, y_2, \dots, y_n find P, x_1, x_2, \dots, x_n

Dew Point Temperature:

Given a vapor composition at a specified pressure, find the composition of the liquid in equilibrium

Given P, y_1, y_2, \dots, y_n find T, x_1, x_2, \dots, x_n

Bubble Point Pressure:

Given a liquid composition at a specified temperature, find the composition of the vapor in equilibrium

Given T, x_1, x_2, \dots, x_n find P, y_1, y_2, \dots, y_n

Bubble Point Temperature:

Given a liquid composition at a specified pressure, find the composition of the vapor in equilibrium

Given P, x_1, x_2, \dots, x_n find T, y_1, y_2, \dots, y_n

Constraints

Raoult's law: 2 unknowns 1 equation

$$\sum_{i=1}^c x_i = 1 \quad \text{and} \quad \sum_{i=1}^c y_i = 1$$

$$\log_{10} P = A - \frac{B}{t + C}$$

Antoine equation for
calculating vapor pressure at
given temperature

BUBL P Calculation (T , x_1 known)

- Calculate P_1^{sat} and P_2^{sat} from Antoine's Equation
- For the vapor-phase composition (bubble) we can write:

$$y_1 + y_2 = 1 \quad (3)$$

- Substitute y_1 and y_2 in Eqn (3) by using Raoult's law:

$$y_i P = x_i P_i^{\text{sat}} \quad (i = 1, 2, \dots, N)$$

$$\frac{x_1 * P_1^{\text{sat}}}{P} + \frac{x_2 * P_2^{\text{sat}}}{P} = \frac{x_1 * P_1^{\text{sat}}}{P} + \frac{(1 - x_1) * P_2^{\text{sat}}}{P} = 1 \quad (4)$$

- Re-arrange and solve Eqn. (4) for P
- Now you can obtain y_1 from Eqn (1)
- Finally, $y_2 = 1 - y_1$

DEW P Calculation (T, y_1 known)

- Calculate P_1^{sat} and P_2^{sat} from Antoine's Equation
- For the liquid-phase composition (dew) we can write:

$$x_1 + x_2 = 1 \quad (5)$$

- Substitute x_1 and x_2 in Eqn (5) by using Raoult's law:

$$\frac{y_1 * P}{P_1^{\text{sat}}} + \frac{y_2 * P}{P_2^{\text{sat}}} = \frac{y_1 * P}{P_1^{\text{sat}}} + \frac{(1 - y_1) * P}{P_2^{\text{sat}}} = 1 \quad (6)$$

- Re-arrange and solve Eqn. (6) for P
- Now you can obtain x_1 from Eqn (1)
- Finally, $x_2 = 1 - x_1$

BUBL T Calculation (P , x_1 known)

Since T is an unknown, the saturation pressures for the mixture components cannot be calculated directly. Therefore, calculation of T , y_1 requires an iterative approach, as follows:

- Re-arrange Antoine's equation so that the saturation temperatures of the components at pressure P can be calculated:

$$T_i^{sat} = \frac{B_i}{A_i - \ln(P)} - C_i \quad (7)$$

- Select a temperature T' so that $T_1^{sat} < T' < T_2^{sat}$

- Calculate $P_1^{sat}(T')$ and $P_2^{sat}(T')$

- Solve Eqn. (4) for pressure P'

$$x_1 * P_1^{sat} + (1 - x_1) * P_2^{sat} = P'$$

- If $|P - P'| < \varepsilon$, then $P' = P$; If not, try another T' -value

Calculate y_1 from Raoult's law

DEW T Calculation (P , y_1 known)

Same as before, calculation of T , x_1 requires an iterative approach:

- Re-arrange Antoine's equation so that the saturation temperatures of the components at pressure P can be calculated from Eqn. (7):
- Select a temperature T' so that $T_1^{sat} < T' < T_2^{sat}$
- Calculate $P_1^{sat}(T')$ and $P_2^{sat}(T')$ from Antoine's Eqn.
- Solve Eqn. (6) for pressure P'
- If $|P - P'| < \varepsilon$ then $P' = P$; If not, try another T' -value
- Calculate x_1 from Raoult's law
$$\frac{y_1 * P}{P_1^{sat}} + \frac{y_2 * P}{P_2^{sat}} = \frac{y_1 * P}{P_1^{sat}} + \frac{(1 - y_1) * P}{P_2^{sat}} = 1$$

Henry's law

For a species present as a very dilute solute in the liquid phase, the partial pressure of the species in the vapor phase is directly proportional to its liquid-phase mole fraction:

$$y_i P = x_i H_i$$

Table 10.1: Henry's Constants for Gases Dissolved in Water at 25°C

Gas	\mathcal{H}/bar	Gas	\mathcal{H}/bar
Acetylene	1,350	Helium	126,600
Air	72,950	Hydrogen	71,600
Carbon dioxide	1,670	Hydrogen sulfide	550
Carbon monoxide	54,600	Methane	41,850
Ethane	30,600	Nitrogen	87,650
Ethylene	11,550	Oxygen	44,380

Henry's law

- ❑ Limiting law applicable to extremely dilute solutions
- ❑ Not applicable for solutions where solute and solvent react
- ❑ Henry's law is applicable for solute and Raoult's law is for solvent over solution

VLE by Modified Raoult's Law

A more realistic equation for VLE, where account is taken of deviation from solution ideality

A factor γ is inserted and Raoult's law is modified as:

$$y_i P = x_i \gamma_i P_i^{sat} \quad (i = 1, 2, \dots, N)$$

where, factor γ is called an ***activity coefficient***

Activity coefficients are functions of temperature and liquid-phase composition.

VLE from *K*-value Correlations

K-value → Defined as measure of the tendency of a given chemical species to partition itself preferentially between liquid and vapor phases

$$K_i \equiv \frac{y_i}{x_i}$$

(Distribution coefficient)

- Use of *K*-value allow elimination of one of the mole fractions
- It serve as the measure of 'lightness' of the constituent species (it's tendency to favor the vapor phase)


- K -value for Raoult's law

$$K_i = \frac{P_i^{sat}}{P}$$


- K -value for Modified Raoult's law

$$K_i = \frac{\gamma_i P_i^{sat}}{P}$$

- Other relations

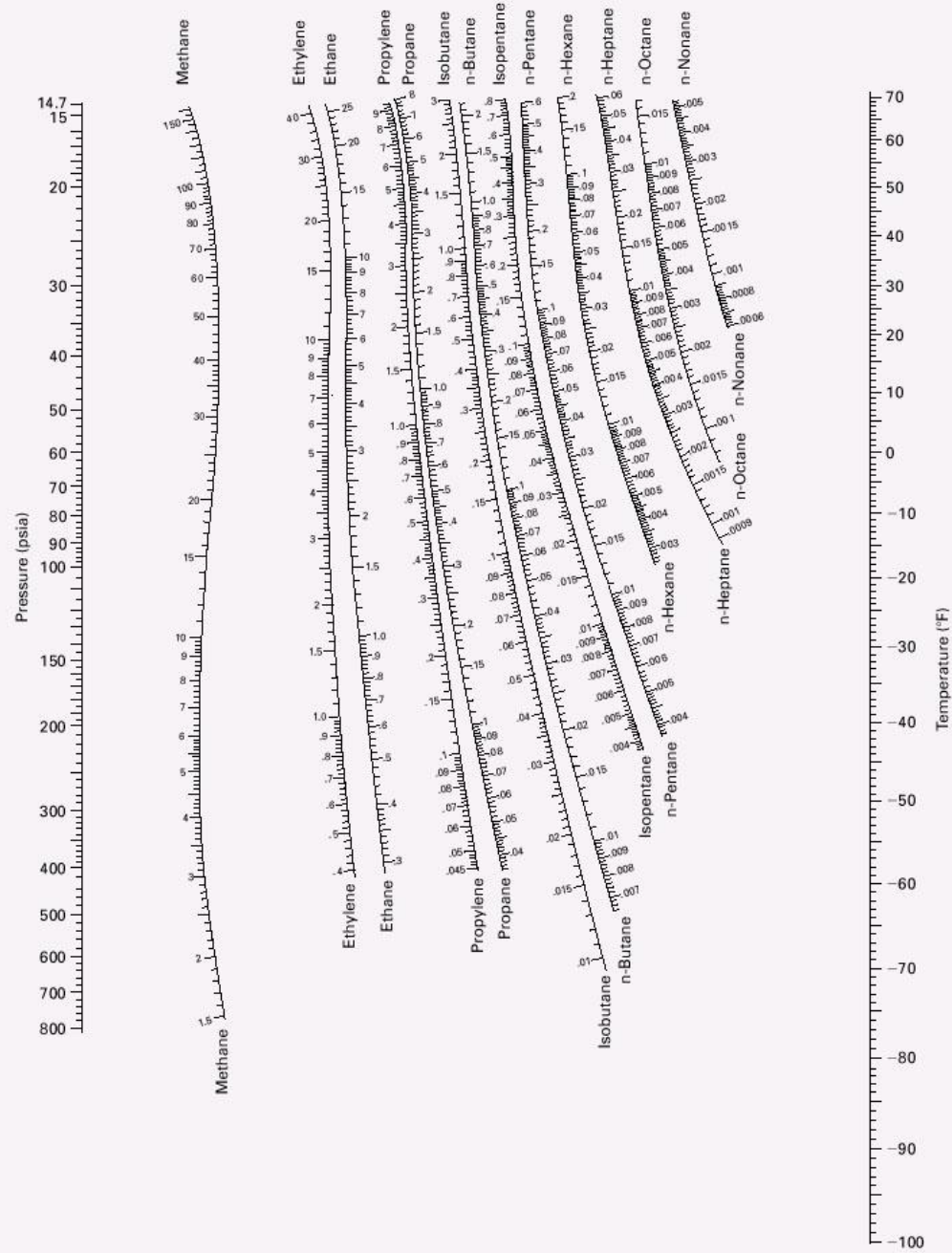

$$\sum K_i x_i = 1$$

Bubble point calculation

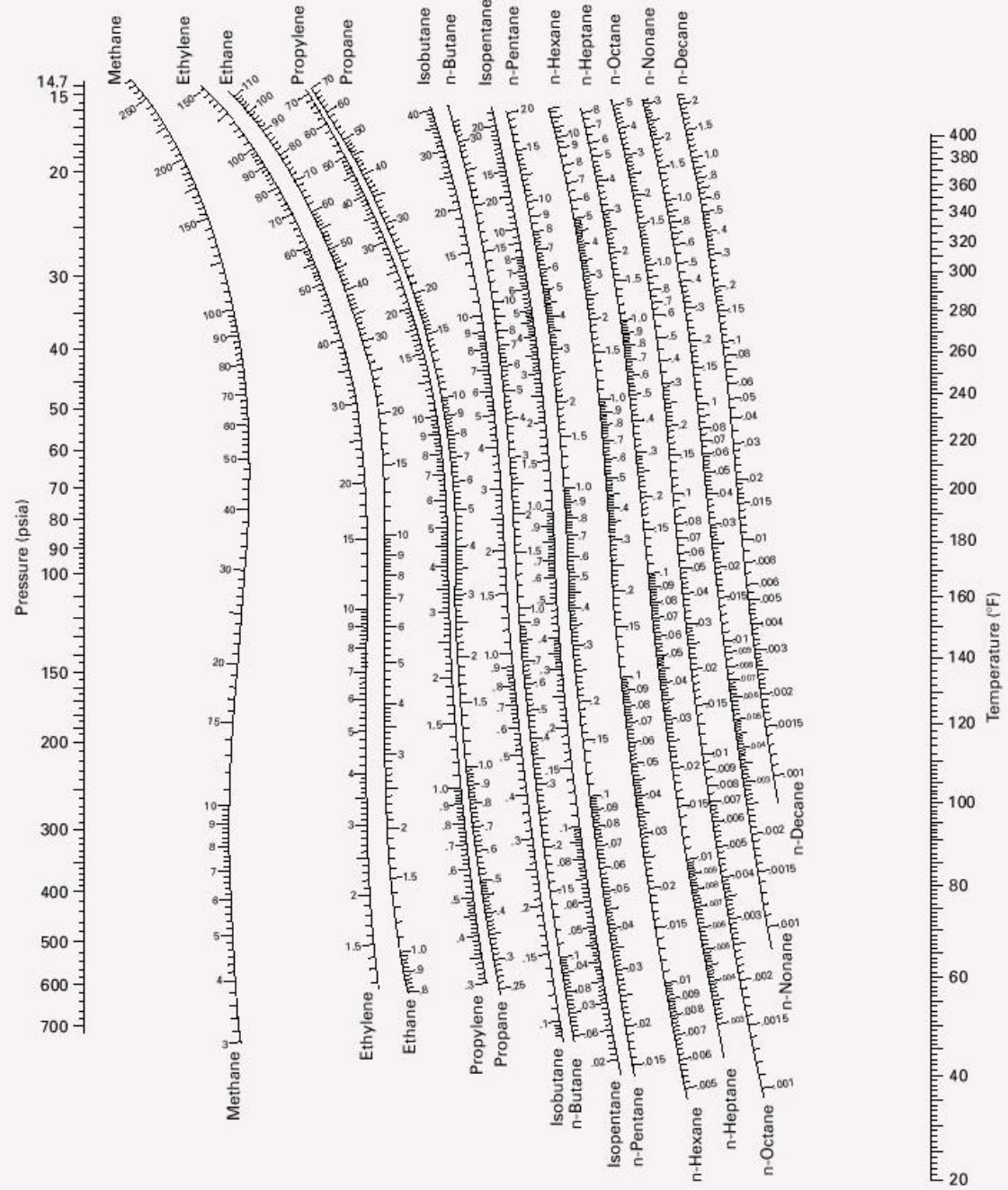
$$\sum \frac{y_i}{K_i} = 1$$


Dew point calculation

K-value chart for light hydrocarbons at low temperature



K-value chart for light hydrocarbons at high temperature



FLASH CALCULATIONS

Flash calculations are important application of VLE

Consider a system containing one mole of mixture of chemical species with an *overall composition represented by the set of mole fractions z_i* . Let L and V be the moles of liquid and vapour formed per mole of feed. The corresponding stream compositions are denoted as x_i and y_i respectively. Material balance equations are:

$$F = L + V = 1$$

$$z_i F = x_i L + y_i V$$

$$z_i = x_i(1 - V) + y_i V$$

Now: $K_i = y_i / x_i = P_i^s / P$

Putting $x_i = y_i / K_i$

$$y_i = \frac{z_i K_i}{1 + V(K_i - 1)}$$

$$\sum y_i = 1$$

$$\sum_i \frac{z_i K_i}{1 + V(K_i - 1)} = 1 \quad (i = 1, 2, \dots, N)$$

Since $x_i = y_i / K_i$, an alternative equation is:

$$x_i = \frac{z_i}{1 + V(K_i - 1)} \quad (i = 1, 2, \dots, N)$$

It follows that: $\sum_i \frac{z_i}{1 + V(K_i - 1)} = 1$

Problem 1 (TB 10.3)

Assuming Raoult's Law to apply to the system n-pentane(1)/n-heptane(2),

What are the values of x_1 and y_1 at $t=55^\circ\text{C}$ and $P = (P_1^{\text{sat}} + P_2^{\text{sat}})/2$? For these conditions plot the fraction of system that is vapor V vs. overall composition z_1 .

Problem 2 (TB 10.19)

A binary system of species 1 and 2 consists of vapor and liquid phases in equilibrium at temperature T , for which

- $\ln \gamma_1 = 1.8 x_2^2$ $\ln \gamma_2 = 1.8 x_1^2$
- $P_1^{\text{sat}} = 1.24 \text{ bar}$ $P_2^{\text{sat}} = 0.89 \text{ bar}$

Assuming the validity of modified Raoult's Law

- a) For what range of values of the overall mole fraction z_1 can this two-phase system exist with a liquid mole fraction $x_1 = 0.65$?
- b) What is the pressure P and vapor mole fraction y_1 within this range?
- c) What are the pressure and composition of the azeotrope at temperature T ?

- (a) &(b) Apply Raoult's Law to calculate P and y_1 , z_1 range would be x_1 to y_1 .
(c) At azeotrope $P = y_1 P_1^{\text{sat}} = y_2 P_2^{\text{sat}}$. Find x_1 for satisfying this relation.
Calculate P.

x1	x2	gama 1	gama 2	gama 1*P1 sat	gama 1*P1 sat	P_cal
0.1	0.9	4.297356	1.018163	5.328721707	0.906165049	3.117443
0.2	0.8	3.164516	1.074655	3.923999364	0.956443256	2.440221
0.3	0.7	2.415726	1.17586	2.99550065	1.046515615	2.021008
0.4	0.6	1.911714	1.333757	2.370524834	1.187044001	1.778784
0.5	0.5	1.568312	1.568312	1.94470711	1.395797845	1.670252
0.51	0.49	1.540612	1.597085	1.910359377	1.421405518	1.665882
0.52	0.48	1.513947	1.626971	1.877294003	1.448004184	1.662649
0.53	0.47	1.488278	1.658013	1.845465187	1.475631721	1.660548
0.54	0.46	1.463572	1.690256	1.814829238	1.504327845	1.659579
0.55	0.45	1.439794	1.723746	1.785344475	1.534134201	1.659739
0.56	0.44	1.416912	1.758533	1.756971133	1.565094466	1.661033
0.57	0.43	1.394896	1.794668	1.729671281	1.597254446	1.663463
0.58	0.42	1.373717	1.832205	1.703408731	1.63066219	1.667035
0.59	0.41	1.353346	1.8712	1.678148965	1.665368106	1.671759
0.5925	0.4075	1.348376	1.881184	1.671986816	1.674253566	1.67312
0.595	0.405	1.343455	1.891263	1.665884777	1.683224306	1.674555
0.5975	0.4025	1.338583	1.90144	1.659842353	1.692281187	1.676062
0.6	0.4	1.333757	1.911714	1.653859057	1.701425083	1.677642