



## Thermodynamics II

### Lec 2: Vapor Liquid Equilibrium-part 2

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## Content



- *Henry's Law*
- **Modified Raoult's law**
- **Bubble and dew points calculations**



# Simple Models For VLE

## Henry's Law

- Application of Raoult's law to species  $i$  requires a value for  $P_i^{sat}$  at the temperature of application, and thus is not appropriate for a species whose critical temperature is less than the temperature of application.
- If a system of air in contact with liquid water is presumed at equilibrium, then the air is saturated with water.
- The mole fraction of water vapor in the air is usually found from Raoult's law applied to the water with the assumption that no air dissolves in the liquid phase.

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# Simple Models For VLE

Henry's Law is VLE relation that is valid for ideal-gas mixture in equilibrium with a dilute solution, where we want to know the composition of dissolved gas  $i$  in the dilute solution.

- For example,
- CO<sub>2</sub> and H<sub>2</sub>O system.
  - Air and H<sub>2</sub>O system.

$$\hat{\phi}_i^1 y_i P = \gamma_i x_i f_i$$

$$y_i P = x_i \gamma_i f_i = x_i \gamma_i P_i^{sat}$$

let  $H_i = \gamma_i f_i = \gamma_i P_i^{sat}$

no value for dissolved (supercritical) gas at VLE conditions



$H_i$  is Henry's constant (in bar) for dissolved gas ( $i$ ).

so  $y_i P = x_i H_i$  Henry's Law  $H_i$  is Henry's constant. come from experiment.

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## Simple Models For VLE

$$y_i P = x_i H_i$$

So at dilute solution,  
 $y_i = (H_i/P) x_i$

For constant system pressure P,  
 $y_i = (\text{Constant})x_i$

If we plot  $y_i$  vs  $x_i$ , we get a straight line through the origin.

So Henry's constant for dissolved gas ( $i$ ) can be easily determined from experiment.

**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



## Simple Models For VLE

- If we wish to calculate the mole fraction of air dissolved in the water, the Raoult's law cannot be applied, because the critical temperature of air is much lower than surrounding temperature.
- This problem can be solved by Henry's law:  $y_i P = x_i H_i$
- Henry's law applied
- For pressures low enough that the vapor phase may be assumed an ideal gas
- For a species present as a very dilute solute in the liquid phase, Henry's law then states that the partial pressure of the species in the vapor phase is directly proportional to its liquid-phase mole fraction

### Example

calculate the mole fraction of air dissolved in the water at 25°C





## Example Air(1) / water(2) system

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## Example 10.2 CO<sub>2</sub> (1) / water (2)

**Compositions of the vapor and liquid phases in sealed soda bottle and the pressure exerted at 283.15 K (10°C)?**

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## Modified Raoult's law

- The solution nonideality in the liquid phase is taken into account

$$y_i P = x_i \gamma_i P_i^{sat} \quad \gamma_i \text{ activity coefficient}$$

There may be severe nonideality in solutions even at low pressures

- Activity coefficients are functions of temperature and liquid phase composition
- Dependence on pressure is usually neglected

$$P = \sum_i x_i \gamma_i P_i^{sat} \quad \text{for BUBL calculations}$$

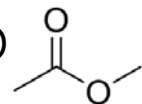
$$P = \frac{1}{\sum_i y_i / \gamma_i P_i^{sat}} \quad \text{for Dew calculations}$$

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## Example

Example 10.3 methanol (1) / methyl acetate (2) (methyl ethanoate)



$$\ln \gamma_1 = Ax_2^2 \quad \ln \gamma_2 = Ax_1^2 \quad A = 2.771 - 0.00523T$$

Antoine equations for vapor pressures

	methanol	methyl acetate
A	16.5785	14.2456
B	3638.27	2662.78
C	239.5	219.69

- (BUBL P)  $P$  and  $y_i$  for  $T = 318.15$  K and  $x_1 = 0.25$
- (DEW P)  $P$  and  $x_i$  for  $T = 318.15$  K and  $y_1 = 0.60$  need iterations
- (BUBL T)  $T$  and  $y_i$  for  $P = 101.3$  kPa and  $x_1 = 0.85$  need iterations
- (DEW T)  $T$  and  $x_i$  for  $P = 101.3$  kPa and  $y_1 = 0.4$  need iterations
- azeotrope

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## Example Cont.

(BUBL P)  $P$  and  $y_i$  for  $T = 318.15$  K and  $x_1 = 0.25$



## Example Cont.

➤ (DEW P)  $P$  and  $x_i$  for  $T = 318.15$  K and  $y_1 = 0.60$       **need iterations**



## Example Cont.

➤ Use the values of  $x_1$  and  $x_2$  to calculate  $\gamma_1$  and  $\gamma_2$

```
gam1 = exp( A * x2 * x2 ) ;
gam2 = exp( A * x1 * x1 ) ;
```

Step 4

➤ And repeat steps 1-4 to get conversion

iter	P	x1	x2	gam1	gam2
0	51.09	0.6887	0.3113	1.0000	1.0000
1	63.64	0.7706	0.2294	1.1133	1.6906
2	62.99	0.8011	0.1989	1.0600	1.9298
3	62.90	0.8116	0.1884	1.0448	2.0349
4	62.89	0.8152	0.1848	1.0401	2.0736
5	62.89	0.8163	0.1837	1.0385	2.0868
6	62.89	0.8167	0.1833	1.0380	2.0913
7	62.89	0.8169	0.1831	1.0379	2.0927
8	62.89	0.8169	0.1831	1.0378	2.0932



## Example Cont.

(BUBL T)  $T$  and  $y_i$  for  $P = 101.33$  kPa and  $x_1 = 0.85$



## Example Cont.



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## Example Cont.



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## Example Cont.

To correct the temperature guess, an expression is required to move the iteration process forward. One of the components (in this example water) is chosen and its pure component vapor pressure at the new temperature is predicted using an iteration formula, which for the bubble point calculation is

$$P_{\text{H}_2\text{O},T_{\text{new}}}^{\text{sat}} = \frac{P_{\text{total}}}{\sum x_i \gamma_i P_i^{\text{sat}}} \cdot P_{\text{H}_2\text{O},T_{\text{old}}}^{\text{sat}}$$

- Solve for new T (using one of the vapour pressure-temperature equations:

Find a new value for  $T$  from the Antoine equation written for species 1:

$$T = \frac{B_1}{A_1 - \ln P_1^{\text{sat}}} - C_1$$



## Example Cont.

With a new value of the temperature, the process of calculating the activity coefficients and partial pressures of the components is continued until...

$$T_{\text{new}} - T_{\text{old}} < \text{Tolerance (e.g. 0.001)}$$



## Example

Example of a Bubble Temperature Calculation, for the system Isopropyl-alcohol(1) & water (2) at a pressure of 150 000 Pa  
The following values will be used throughout the example:

mole fraction IPA =  $x_1 = 0.35$

mole fraction water =  $x_2 = 0.65$

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## Example Cont.

The activity coefficients from the NRTL model are given by the equations

$$\ln \gamma_1 = x_2^2 \left[ \tau_{21} \left( \frac{G_{21}}{x_1 + x_2 G_{21}} \right)^2 + \frac{G_{12} \tau_{12}}{(x_2 + x_1 G_{12})^2} \right]$$

$$\ln \gamma_2 = x_1^2 \left[ \tau_{12} \left( \frac{G_{12}}{x_2 + x_1 G_{12}} \right)^2 + \frac{G_{21} \tau_{21}}{(x_1 + x_2 G_{21})^2} \right]$$

where

$$G_{12} = e^{-\alpha \tau_{12}} \quad \tau_{12} = \frac{A_{12}}{RT}$$

$$G_{21} = e^{-\alpha \tau_{21}} \quad \tau_{21} = \frac{A_{21}}{RT}$$

$$A_{12} = 1179.9 \text{ J mol}^{-1} \quad A_{21} = -422.91 \text{ J mol}^{-1} \quad \alpha = 0.2$$

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## Example Cont.

To Calculate the initial temperature guess, the pure component vapor pressure equations are used, for the IPA

$$\ln P_{\text{sat}} = 88.134 - \frac{8498.6}{T} - 9.0766 \ln T + 8.3303 \times 10^{-18} T^6$$

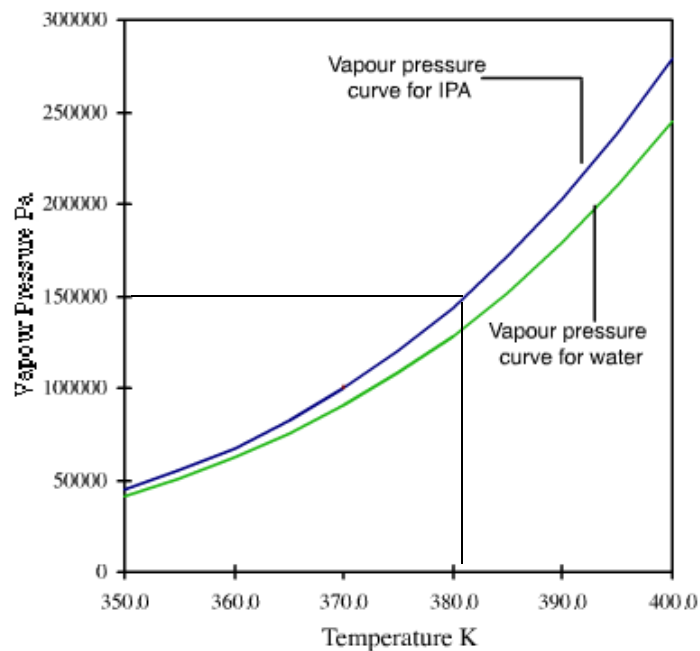
and for the water

$$\ln P_{\text{sat}} = 73.649 - \frac{7258.2}{T} - 7.3037 \ln T + 4.1653 \times 10^{-6} T^2$$



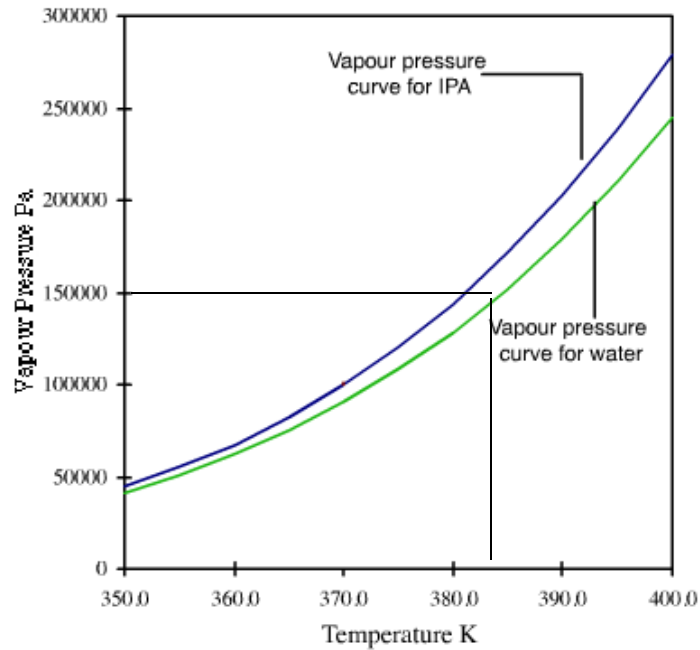
## Example Cont.

From the graph, the temperature at which the vapor pressure of IPA is 150000 Pa is found as



## Example Cont.

The temperature at which the vapor pressure of water is 150 000 Pa is found in  $t^{\circ}$



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## Example Cont.

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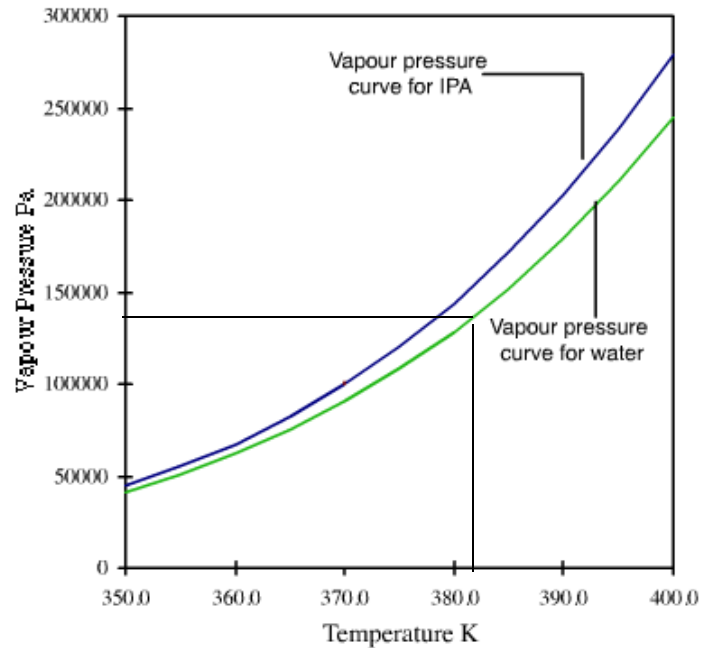
## Example Cont.



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## Example Cont.



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## Example Cont.

With a new value of the temperature, the process of calculating the activity coefficients and partial pressures of the components is continued until...

$$T_{\text{new}} - T_{\text{old}} < \text{Tolerance (e.g. 0.001)}$$

Move on to the last page to watch the calculation converge

In the table below are the values of the vapour pressures, and the temperature guesses as the iteration proceeds.

Iteration	$x_1$	$x_2$	$T_{\text{guess}}$	$P_1^{\text{sat}}$	$P_2^{\text{sat}}$	$\sum x_i \gamma_i P$	New $P^{\text{sat}}$
1	0.35	0.65	383.4	162209	144329	155390	139323
2	0.35	0.65	382.4	156409	139322	149942	139376
3	0.35	0.65	382.4	156464	139369	149994	139375

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