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.

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 dissolve gas *i* in the dilute solution.

For example, a) CO_2 and H_2O system.

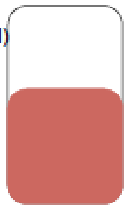
b) Air and H_2O system.

$$\hat{\phi}_i y_i P = \gamma_i x_i f_i \quad (\hat{\phi}_i = 1)$$

no value for dissolved (supercritical) gas at VLE conditions

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

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



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

so $y_i P = x_i H_i$ Henry's Law $\mathcal{H}_i$ *is Henry's constant.* come from experiment,

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,
$y_i = (Constant) x_i$

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 that 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

Example 10.2 CO_2 (1) / water (2)

Compositions of the vapor and liquid phases in sealed soda bottle and the pressure excerted 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

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

γ_i **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

$$P = \sum_i x_i \gamma_i P_i^{sat}$$

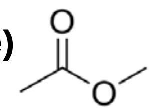
for BUBL calculations

$$P = \frac{1}{\sum_i y_i / \gamma_i P_i^{sat}}$$

for Dew calculations

Example

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



$$\ln \gamma_1 = A x_2^2 \qquad \ln \gamma_2 = A x_1^2 \qquad A = 2.771 - 0.00523T$$

Antoine equations for vapor pressures

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

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

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

(c) (BUBL T) T **and** y_i **for** P **= 101.3 kPa and** $x_1 = 0.85$ **need iterations**

(d) (DEW T) T **and** x_i **for** P **= 101.3 kPa and** $y_1 = 0.4$ **need iterations**

(e) azeotrope

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_i to calculate γ_1 and γ_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.

Example Cont.

Example Cont.

To correct the temperature guess, an expresion 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

$$P^{sat}_{H_2O,T_{new}} = \frac{P_{total}}{\sum x_i \gamma_i P_i^{sat}} \cdot P^{sat}_{H_2O,T_{old}}$$

- 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:

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

Example Cont.

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

$T_{new} - T_{old}$ < Tolerence(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

$$G_{12} = e^{-\alpha\tau 12} \qquad \tau 12 = \frac{A_{12}}{RT}$$

$$G_{21} = e^{-\alpha\tau 21} \qquad \tau 21 = \frac{A_{21}}{RT}$$

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

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Example Cont.

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

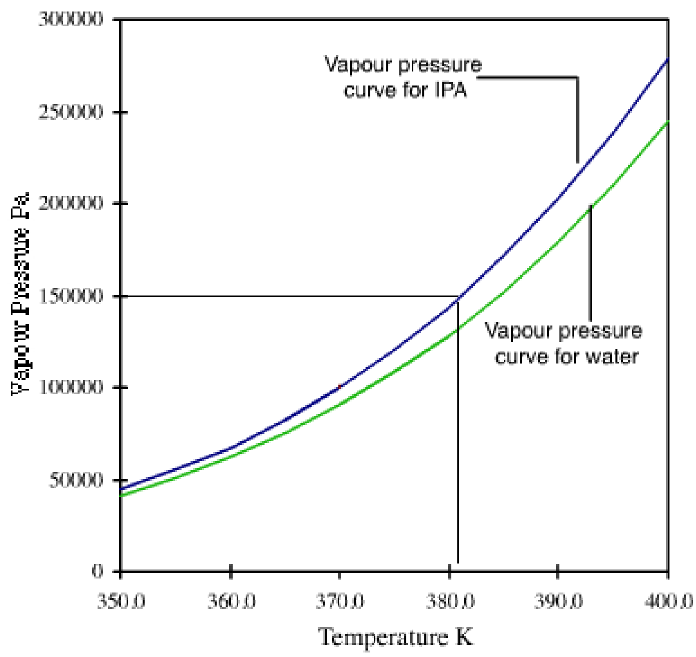
$$\ln P_{sat} = 88.134 - \frac{8498.6}{T} - 9.0766 \ln T + 8.3303 \times 10^{-18} T^6$$

and for the water

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

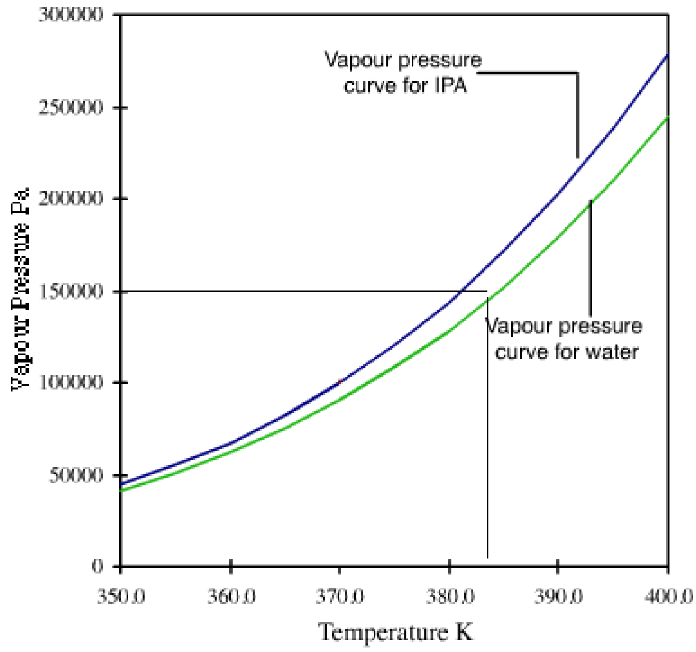
Example Cont.

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



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Example Cont.

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Example Cont.

Example Cont.

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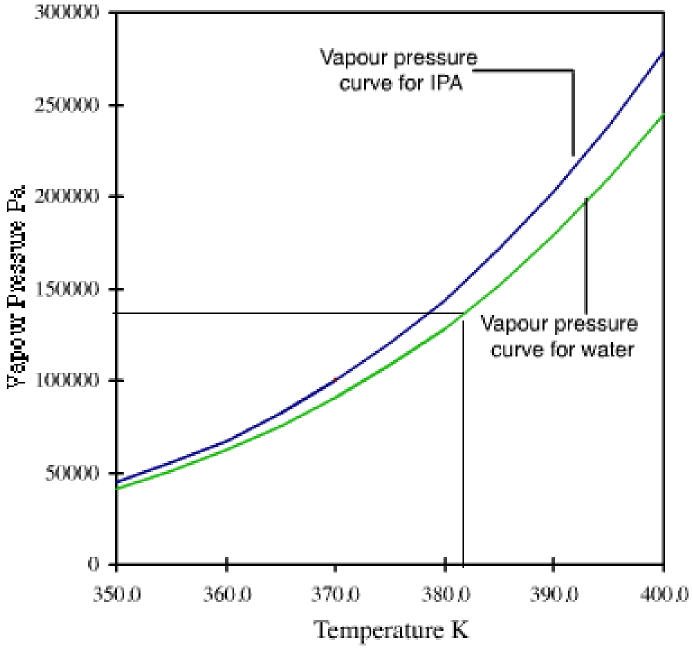

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Example Cont.

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

$T_{new} - T_{old}$ < Tolerence(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 temperaure guesses as the iteration proceeds.

Iteration	x_1	x_2	T_{guess}	P_1^{sat}	P_2^{sat}	$\sum x_i \gamma_i P$	New P^{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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