Lecture General Chemistry
Winter Term 2022/23

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- Website (Slides, Excercises):
- http://www.chemie.uni-siegen.de/pc/lehre/nanoscitec/

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Deviations from ideal behaviour

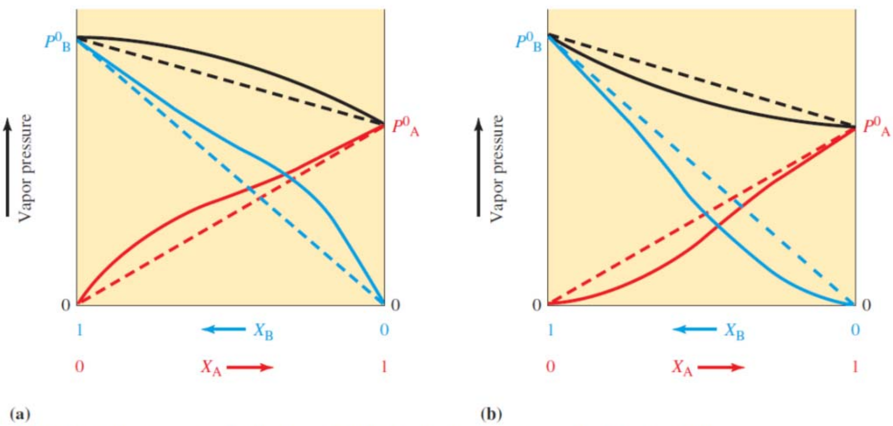
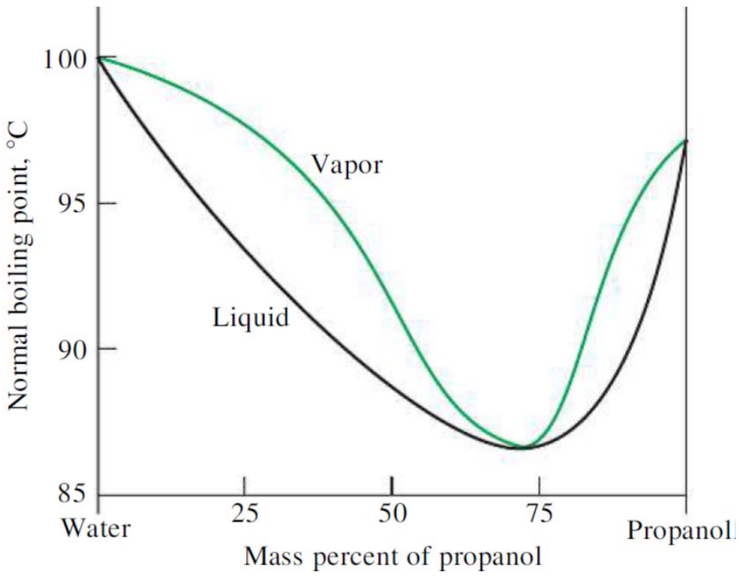


Figure 14-11 Deviations (*solid lines*) from Raoult's Law for two volatile components. Ideal behavior (Raoult's Law) is shown by the dashed lines. (a) Positive deviation. (b) Negative deviation.

Azeotropic mixtures



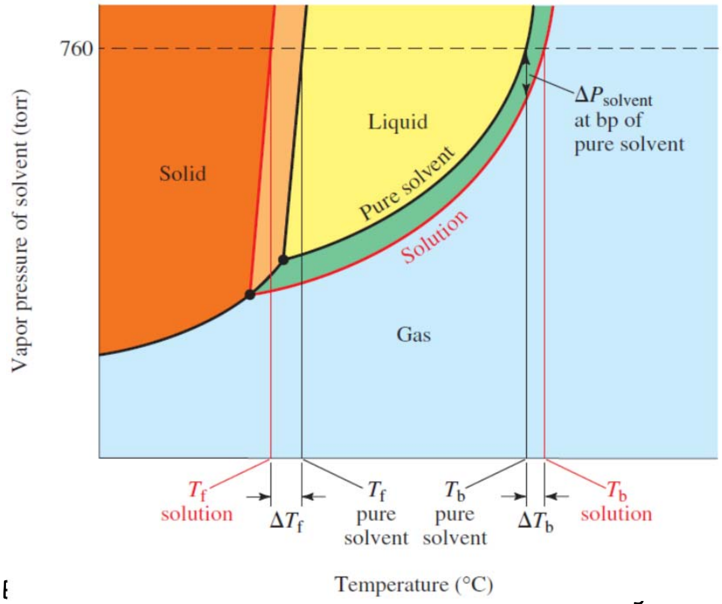
boiling and freezing temperature of solutions

- solution: solvent with solute
- different properties than pure solvent
- boiling point: temperature, where $p_{solvent}$ = 1,013 bar

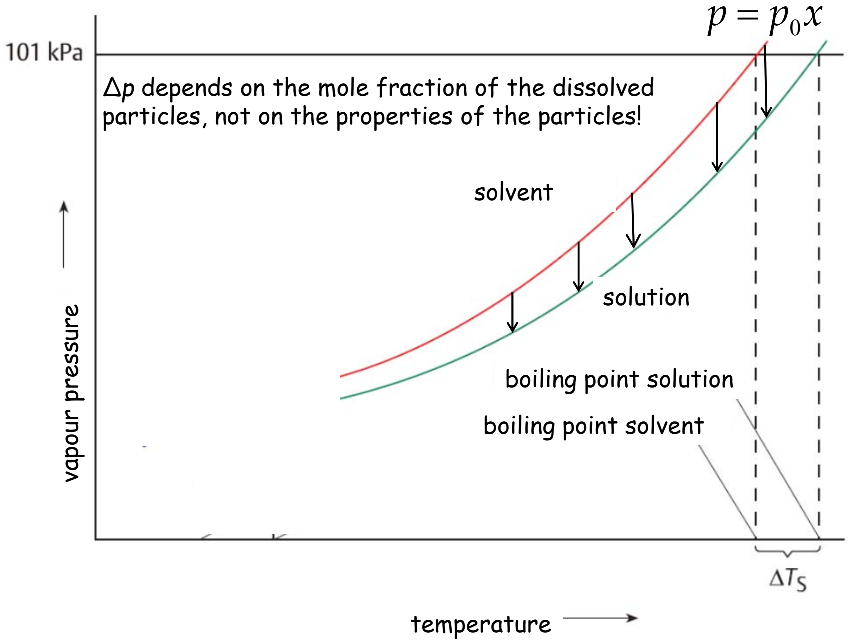
- Raoult's law: $p_{\text{solution}} < p_{\text{solvent}}$

- boiling points of solutions are higher!

Change of boiling and freezing temperature



$p = p_0 x$



- Boiling point elevation

$$\Delta T_S = K_B \overline{m}$$

- K_B : Ebullioskopic constant
- $\overline{m}$: Molality (mol/kg)
- Dissociation: more particles!

Solvent	bp (pure)	K_b (°C/m)
water	100*	0.512
benzene	80.1	2.53
acetic acid	118.1	3.07
nitrobenzene	210.9	5.24
phenol	182	3.56
camphor	207.4	5.61

- Freezing point depression $\Delta T_F = K_F \overline{m}$
  - K_F: Kryoskopic constant
  (d: dissolved, s: solvent)

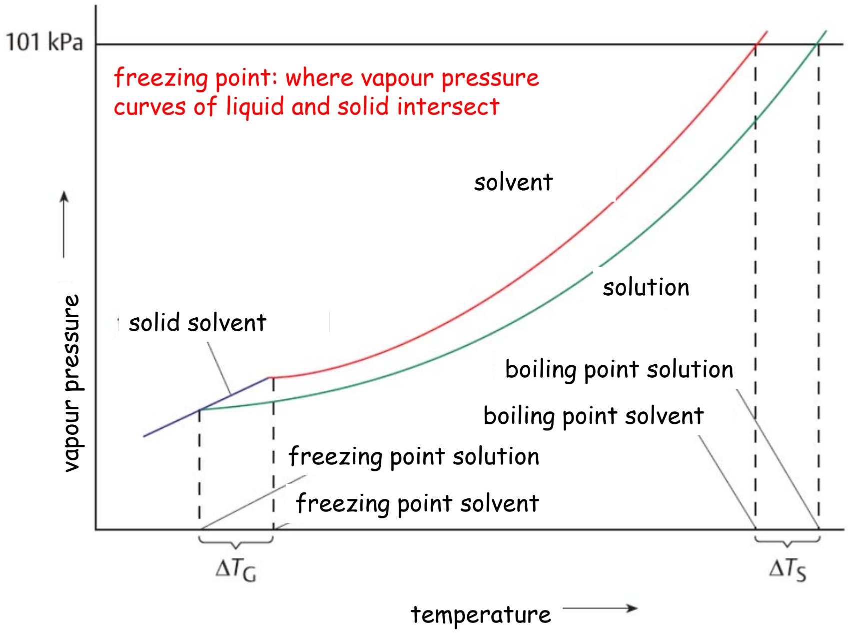
$$\Delta T_F = K_F \overline{m} = K_F \frac{n_d}{m_s} = K_F \frac{m_d}{M_d m_s}$$

$$M_d = \frac{K_F m_d}{\Delta T\, m_s}$$

Solvent	fp (pure)	K_f (°C/m)
water	0*	1.86
benzene	5.5	5.12
acetic acid	16.6	3.90
nitrobenzene	5.7	7.00
phenol	43	7.40
camphor	178.4	40.0

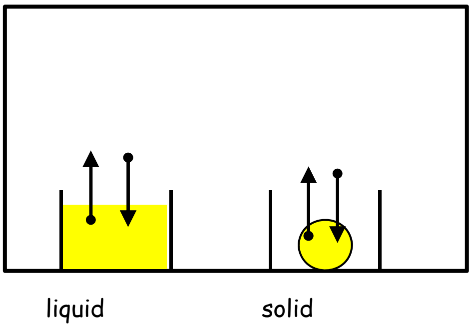
Properties of solutions

- Solubility of solids
- Solubility of gases
- Vapor pressure of solutions
- distillation
- boiling point elevation
- freezing point depression
- Stability condition of phases
- Acids and bases
- Redox-Reactions in solutions



Stability of Phases

thought experiment:



Liquid and solid are in equilibrium with gas phase

after some time the phase with higher vapour pressure is gone

the phase with lower vapour pressure is more stable

Acids and Bases

What are acids, what are bases?

Arrhenius: Acids release protons
Bases release hydroxid ions

Brønstedt: Acids: Proton donators
Bases: Proton akzeptors

some substances can do both: amphoteric substances

$$H_2O \rightarrow H^+ + OH^-$$

Autoprotolysis of water

$H_2O \leftrightarrow H^+ + OH^-$

$$K = \frac{c(\mathrm{H^+})c(\mathrm{OH^-})}{c(\mathrm{H_2O})}$$

if $K \neq 0$, in pure water: $c\,(H^+) = c\,(OH^-) > 0$

Definition: Water is neutral (neither acidic nor basic) if $c\,(H^+) = c\,(OH^-)$

Determination: eg electrochemically: specify $c(OH^-)$, measure $c(H^+)$

$$K = \frac{c(\mathrm{H^+})c(\mathrm{OH^-})}{c(\mathrm{H_2O})}$$

(almost) constant, $c(H_2O)$ = 55,5 mol/L

$$c(\mathrm{H^+})\cdot c(\mathrm{OH^-}) = K\cdot c(\mathrm{H_2O}) = K_w = 1{,}1\cdot 10^{-14} \approx 10^{-14}\,\frac{\mathrm{mol}^2}{\mathrm{L}^2}$$

K_w : Ion product of water

Water at 25 °C is neutral if $c\,(H^+) = c\,(OH^-) = 10^{-7}$ mol/L

What about other temperatures?
(Le Chatelier /Braun)

T/°C	pH	*T*/°C	pH
0	7,47	30	6,92
10	7,27	37	6,81
20	7,08	50	6,63
25	7,00	100	6,13

Determination of the ion product of the water

(Explanation in Chapter Electrochemistry)

$$\mathrm{Pt}\,|\,\mathrm{H_2}, 1{,}013\ \mathrm{bar}\,|\,0{,}01\ \mathrm{M\ HCl}\,|\,\mathrm{KNO_3\text{-}Lsg}\,|\,0{,}01\ \mathrm{M\ KOH}\,|\,\mathrm{H_2}, 1{,}013\ \mathrm{bar}\,|\,\mathrm{Pt}$$

At 25 °C one finds E = -0,5874 V

$$E = 0 - 0{,}059\,\mathrm{V}\,\lg\frac{c_{\mathrm{H^+,links}}}{c_{\mathrm{H^+,rechts}}} = -0{,}059\,\mathrm{V}\,\lg\frac{c_{\mathrm{H^+,links}}\cdot c_{\mathrm{OH^-,rechts}}}{K_\mathrm{W}}$$

$$K_\mathrm{W} = \frac{10^{-4}}{10^{0{,}5874/0{,}059}} = 1{,}1\cdot 10^{-14}\ \mathrm{mol^2/dm^6}$$

pH, pOH and pK_A

$\mathrm{pH} = -\lg c(\mathrm{H^+})$ $\mathrm{pOH} = -\lg c(\mathrm{OH^-})$ $\mathrm{p}K_A = -\lg K_A$

at 25 °C one finds: $c(\mathrm{H^+})\cdot c(\mathrm{OH^-}) = 10^{-14}\,\frac{\mathrm{mol}^2}{\mathrm{L}^2}$

therefor: pH + pOH = 14

for neutral Water: pH = pOH = 7

pK_A-values of some acid-base pairs at 25 C

increasing strenght of acid

Säure	Base	pK_s
$HClO_4$	ClO_4^-	-10
HCl	Cl^-	- 7
H_2SO_4	HSO_4^-	- 3,0
H_3O^+	H_2O	- 1,74
HNO_3	NO_3^-	- 1,37
HSO_4^-	SO_4^{2-}	+ 1,96
H_2SO_3	HSO_3^-	+ 1,90
H_3PO_4	$H_2PO_4^-$	+ 2,16
$[Fe(H_2O)_6]^{3+}$	$[Fe(OH)(H_2O)_5]^{2+}$	+ 2,46
HF	F^-	+ 3,18
CH_3COOH	CH_3COO^-	+ 4,75
$[Al(H_2O)_6]^{3+}$	$[Al(OH)(H_2O)_5]^{2+}$	+ 4,97
$CO_2 + H_2O$	HCO_3^-	+ 6,35
$[Fe(H_2O)_6]^{2+}$	$[Fe(H_2O)_5OH]^+$	+ 6,74
H_2S	HS^-	+ 6,99
HSO_3^-	SO_3^{2-}	+ 7,20
$H_2PO_4^-$	HPO_4^{2-}	+ 7,21
$[Zn(H_2O)_6]^{2+}$	$[Zn(H_2O)_5OH]^+$	+ 8,96
HCN	CN^-	+ 9,21
NH_4^+	NH_3	+ 9,25
HCO_3^-	CO_3^{2-}	+10,33
H_2O_2	HO_2^-	+11,65
HPO_4^{2-}	PO_4^{3-}	+12,32
HS^-	S^{2-}	+12,89
H_2O	OH^-	+15,74
OH^-	O^{2-}	+29

increasing strenght of base

Strong and weak acids and bases

Definition: Strong acids and bases dissociate completely

Definition: Weak acids and bases do not completely dissociate, but only (very) little.

For strong acids + bases, the calculation of pH or pOH is simple:

$$\mathrm{pH} = -\lg c_0(\mathrm{HA}) \qquad \mathrm{pOH} = -\lg c_0(\mathrm{BOH})$$

$$\text{for HA} \rightarrow \mathrm{H}^+ + A^- \qquad \text{for BOH} \rightarrow \mathrm{B}^+ + \mathrm{OH}^-$$

A^- : acid residue $\quad$ B^+ : base residue

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pH calculation for weak acids

$$\text{for HA} \rightleftharpoons \text{H}^+ + A^- : \qquad K_A = \frac{c(\text{H}^+)c(\text{A}^-)}{c(\text{HA})}$$

2 simplifications:

1.: weak acids: (very) weak dissociated, therefore $c(\text{HA}) \approx c_0(\text{HA})$

2.: in spite of weak dissociation: $c(\text{H}^+)_{\text{water}} \ll c(\text{H}^+)_{\text{acid}}$

so we have $c(\text{H}^+) \approx c(\text{A}^-)$ and $K_A = \frac{c(\text{H}^+)c(\text{A}^-)}{c(\text{HA})} = \frac{c^2(\text{H}^+)}{c_0(\text{HA})}$

$$c^2(\text{H}^+) = K_A \cdot c_0(\text{HA}) \qquad c(\text{H}^+) = \sqrt{K_A \cdot c_0(\text{HA})}$$

logarithmic form: $\text{pH} = \frac{1}{2}(\text{pK}_\text{A} - \lg c_0(\text{HA}))$

How far do weak acids dissociate?

$$\text{for HA} \rightleftharpoons \text{H}^+ + \text{A}^- : \qquad K_A = \frac{c(\text{H}^+)c(\text{A}^-)}{c(\text{HA})}$$

Calculated for Acetic Acid and $K_A = 1{,}8 \cdot 10^{-5}$ mol L^{-1}

$$c(\text{H}^+) = \sqrt{K_A \cdot c_0(\text{HA})}$$

c_0 /mol L^{-1}	c(H^+) /mol L^{-1}	pH
10^{-1}	$1{,}3 \cdot 10^{-3}$	2,9
10^{-3}	$1{,}3 \cdot 10^{-4}$	3,9
10^{-5}	$1{,}3 \cdot 10^{-5}$	4,9

Do the assumptions still apply here?

For c_0 = 3,6 10^{-5} mol/l we get 50% dissoziation

so pH = -lg(1,8$10^{-5}$) = 4,74

$$K_A = \frac{1{,}8 \cdot 10^{-5} \cdot 1{,}8 \cdot 10^{-5}}{1{,}8 \cdot 10^{-5}} = 1{,}8 \cdot 10^{-5} \frac{\text{mol}}{\text{L}}$$

Degree of dissociation α

$$\alpha = \frac{c(\mathrm{A}^-)}{c_0(\mathrm{HA})} = \frac{c(\mathrm{H}^+)}{c_0(\mathrm{HA})}$$

$$\alpha = \frac{\sqrt{K_A \cdot c_0(\mathrm{HA})}}{c_0(\mathrm{HA})} \quad = \sqrt{\frac{K_A}{c_0(\mathrm{HA})}}$$

Calculation of buffer systems

$$K_A = \frac{c(\mathrm{H}^+)c(\mathrm{A}^-)}{c(\mathrm{HA})} \quad = c(\mathrm{H}^+)\frac{c(\mathrm{A}^-)}{c(\mathrm{HA})}$$

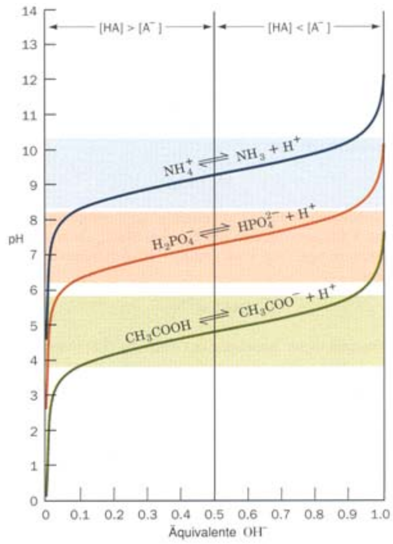
logarithmize, then multiply by -1:

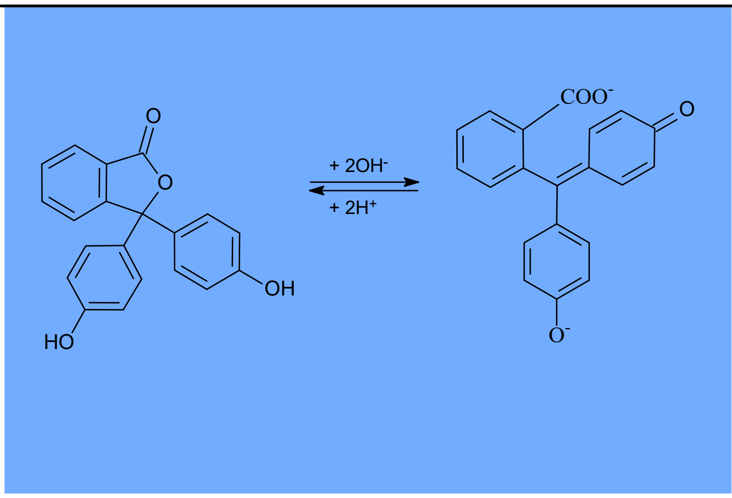
$$-\lg K_A = -\lg c(\mathrm{H}^+) - \lg\frac{c(\mathrm{A}^-)}{c(\mathrm{HA})}$$

$$\mathrm{pK_A} = \mathrm{pH} - \lg\frac{c(\mathrm{A}^-)}{c(\mathrm{HA})} \qquad \mathrm{pH} = \mathrm{pK}_A + \lg\frac{c(\mathrm{A}^-)}{c(\mathrm{HA})}$$

$$\mathrm{pH} = \mathrm{pK}_A \ \text{ for } c(\mathrm{A}^-) = c(\mathrm{HA})$$

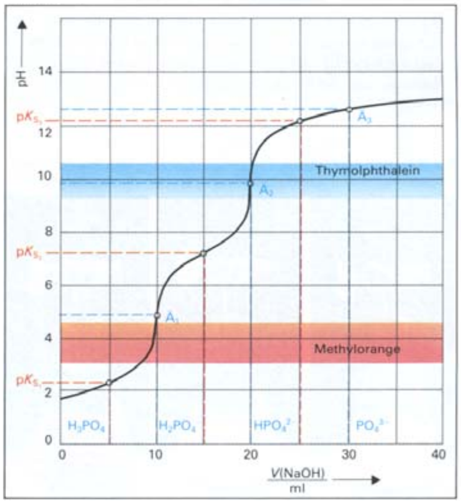
Buffered titration curves





„measuring pH"
Indicator molecule Phenolphthalein:
colorless in acidic and neutral solutions
pink in strong acidic solutions

Titration curve for H_3PO_4



$$AH_3 \rightleftharpoons H^+ + AH_2^-$$

$$AH_2^- \rightleftharpoons H^+ + AH^{2-}$$

$$AH^{2-} \rightleftharpoons H^+ + A^{3-}$$