Chemistry 163B
Lecture 26- Concluding Factoids W2014

Chemistry 163B

Concluding Factoids

and

Comments

1

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http://projects.gw.utwente.nl/pi/sim/Bovt/concep4.gif

http://www.uta.edu/biology/westmoreland/classnotes/1442/Chapter_48_files/image009.jpg

2

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resting potential and Nernst Equaiton

major source of potential: $[K^+]_{outside}(C_{out}) \rightleftarrows [K^+]_{inside}(C_{in})$

$$\Phi = \Phi^\circ - \frac{RT}{n\mathcal{F}}\ln Q$$

$$\Phi^\circ = 0$$

$$Q = \frac{[K^+]_{inside}}{[K^+]_{outside}}$$

$$\Phi = -\frac{RT}{n\mathcal{F}}\ln Q = -.02569\ln\frac{[K^+]_{inside}}{[K^+]_{outside}}$$

$$= -.02569\ln\frac{140\ mM}{5\ mM} = -0.086\ V$$

Typical Ion Concentrations Inside and Outside of Nerve Cells

Ion	Concentration Inside	Concentration Outside
Sodium (Na^+)	12 mM	145 mM
Potassium (K^+)	140 mM	5 mM
Calcium (Ca^{++})	0.1 μM	2 mM

**The computed number is a little higher than the quantity measured
in experiments (-70 mV) but all the factors in this complex physical process
have been accounted for**. http://www.medicalcomputing.net/action_potentials.html

$$E_{rev} = \frac{R \cdot T}{z \cdot F}\left[\frac{P_K \cdot [K]_o + P_{Na} \cdot [Na]_o + P_{Cl} \cdot [Cl]_i}{P_K \cdot [K]_i + P_{Na} \cdot [Na]_i + P_{Cl} \cdot [Cl]_o}\right]$$

http://www.cartho.ucsd.edu/faculty/hartline/models.htm

3

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vocabulary

Gibbs-Duhem

the partial molar quantities do not vary independently

4

Gibbs-Duhem

$$X_{EtOH}\left(\frac{\partial \overline{V}_{EtOH}}{\partial n_{EtOH}}\right)_{T,P,n_{H_2O}} = -X_{H_2O}\left(\frac{\partial \overline{V}_{H_2O}}{\partial n_{EtOH}}\right)_{T,P,n_{H_2O}}$$

what are

$$\left(\frac{\partial \overline{V}_a}{\partial n_a}\right)_{T,P,n_b} \quad and \quad \left(\frac{\partial \overline{V}_b}{\partial n_a}\right)_{T,P,n_a}$$

when a and b
form an ideal solution ?

do ideal
solutions
obey the
Gibbs-Duhem
relation?

http://www.chem.unt.edu/faculty/cooke/3510/3510_chap7.ppt

5

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non-ideal solutions

6

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benzene-toluene, quite ideal (similar to Fig 9.2 E&R) !!

Raoult's Law of Ideal Solutions

$$P_A = X_A^{(\ell)} P_A^\bullet \qquad P_B = X_B^{(\ell)} P_B^\bullet$$

$$P_{total} = X_A^{(\ell)} \left(P_A^\bullet - P_B^\bullet \right) + P_B^\bullet$$

Benzene and Toluene

http://www.chem.ucsb.edu/coursepages/06fall/1C-Watts/dl/Lecture_Notes/Lecture16.%2011-8-06Colligative%20Properties%20Solutions.pdf

7

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ideal solution: T vs X (P=1 atm) for solution-vapor equilibrium

toluene (b.p.=383.78) + benzene (b.p.=353.25)

tol+ben (vapor)
[f_remaining=2]

solution + vapor
[f_remaining=1]

tol+ben (solution)
[f_remaining=2]

8

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non-ideal solutions: azeotrope

Definition[s]:

• constant boiling liquid

• solution where the mole fraction of each component
  is the same in the liquid (solution) as the vapor

$$X_i^{(\ell)} = X_i^{(v)}$$

• boiling point of azeotrope may be higher or lower
  than of pure liquids

9

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non-ideal solutions: positive deviations from ideal solution (E&R pp 214-218)

$$CS_2(\ell) + (CH_3)_2CO(\ell)$$

• positive deviations from
  Raoult's Law:
  smaller forces between
  components than 'within' components

• total pressure greater than ideal
  solution

FIGURE 9.13
The data in Table 9.3 are plotted
versus x_{CS_2}. The dashed lines show the
expected behavior if Raoult's law were
obeyed.

10

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acetone-carbon disulfide: positive deviation ⇒ low boiling azeotrope

http://www.separationprocesses.com/Distillation/Fig011b.htm

11

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low boiling azeotrope

• weaker between component forces
  (A↔B) (than A↔A, B↔B)

• fractional distillation leads to constant
  boiling azeotrope in vapor

• *and (in pot after azeotrope boils off)*
  • $(X_A)_{initial} > (X_A)_{azeotrope}$ pure A
  • $(X_A)_{initial} < (X_A)_{azeotrope}$ pure B
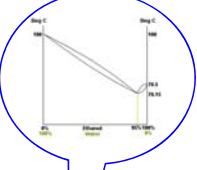
http://www.solvent--recycling.com/azeotrope_1.html

12

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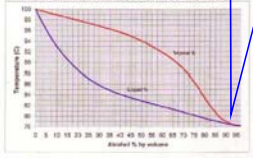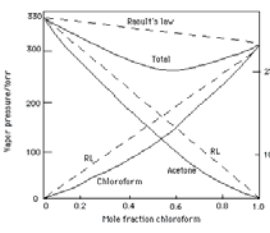
Water-Ethanol Mixture

For the water-ethanol mixture, the azeotrope concentration corresponds to ~95% of ethanol in the mixture. This is the limit that can be reached by distillation of a less-alcohol-rich mixture.

13

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non-ideal solutions : negative deviations from ideal solution
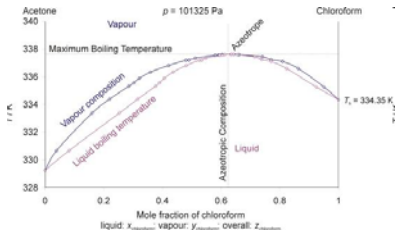
$CHCl_3(\ell) + (CH_3)_2CO(\ell)$

- negative deviations from Raoult's Law: greater forces between components than 'within' components

- total pressure lower than ideal solution

http://dwb4.unl.edu/Chem/CHEM869W/CHEM869WImages/raoult2.gif

14

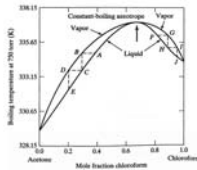*acetone-chloroform: negative deviation ⇨ high boiling azeotrope*

http://www.chm.bris.ac.uk/~chdms/Teaching/Chemical_Interactions/images/pic192.jpg

15

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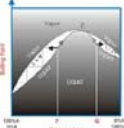
high boiling azeotrope
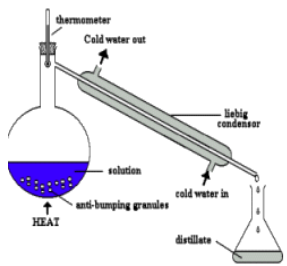
- stronger between component forces (A↔B) (than A↔A, B↔B)

- fractional distillation leads to pure component in vapor until solution (pot) reaches azeotrope composition

  - $(X_A)_{initial} > (X_A)_{azeotrope}$ pure A
  - $(X_A)_{initial} < (X_A)_{azeotrope}$ pure B

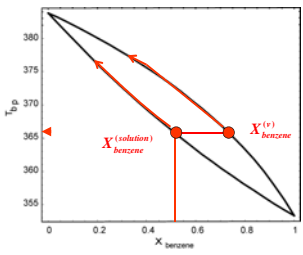http://www.solvent--recycling.com/azeotrope_1.html

16

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simple distillation

http://www.docbrown.info/page12/gifs/distill.gif

17

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simple distillation (one evaporation; T_{bp} varies as X changes)

add heat
$X^{(solution)}_{benzene}$ *decreases*
T_{bp} *increases gradually*

$X^{(solution)}_{benzene}$ $X^{(v)}_{benzene}$

$X_{benzene}$

18

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fractional distillation

http://www.wpbschoolhouse.btinternet.co.uk/page12/gifs/FracDistRed.gif

19

Fractional Distilation

I. • start with 50-50 mixture
   • $T_{bp} \approx 366$

II. • vapor $X^v_{benzene} \approx .72$

III. • condense $X^\ell_{benzene} \approx .72$
    • $T_{bp} \approx 359.5$

IV. • evaporate
    • vapor $X^v_{benzene} \approx .88$

V. etc, ...

VI. apporaches
   $X_{benzene} = 1$

20

T vs progress for a distillation

http://www.uwlax.edu/faculty/koster/Image119.gif

21
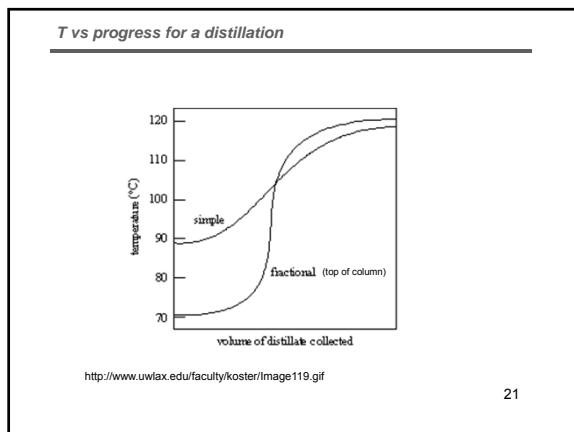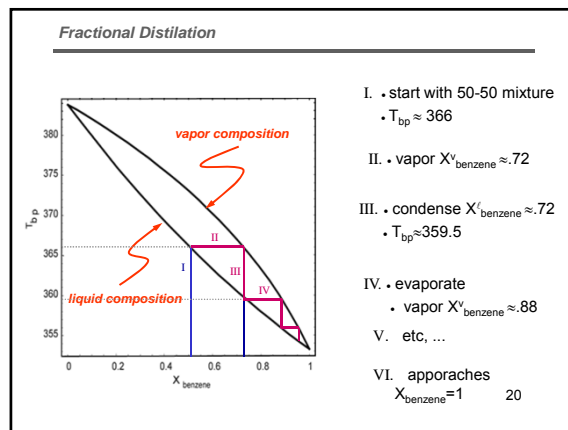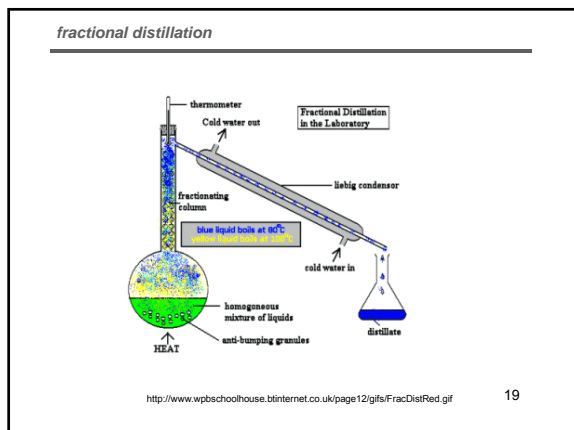
**Electrolytes and
Debye-Huckel Theory**

22

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activity coefficients for ions (HW9 #58)

$$BaCl_2\,(s) \rightleftharpoons Ba^{2+}(aq) + 2Cl^-(aq)$$

$$K_{sp} = \frac{\left(a_{Ba^{2+}(aq)}\right)\left(a_{Cl^-(aq)}\right)^2}{\left(a_{BaCl_2(s)}\right)}$$

$$a_{BaCl_2(s)} = 1$$

$$a_{Ba^{2+}(aq)} = \gamma_{Ba^{2+}}\left[Ba^{2+}\right]$$

$$a_{Cl^-(aq)} = \gamma_{Cl^-}\left[Cl^-\right]$$

cannot determine $\gamma_{Ba^{2+}}$ and γ_{Cl^-} independently

but only $\gamma_{Ba^{2+}} = \gamma_{Cl^-} = \gamma_\pm$ $(\gamma_+ = \gamma_- \equiv \gamma_\pm)$

$$K_{sp} = \frac{(\gamma\pm)^3}{1}\frac{\left([Ba^{2+}]/1M\right)\left([Cl^-]/1M\right)^2}{(1)}$$

$$K_{sp} = (\gamma\pm)^3\left[Ba^{2+}\right]\left[Cl^-\right]^2$$

23
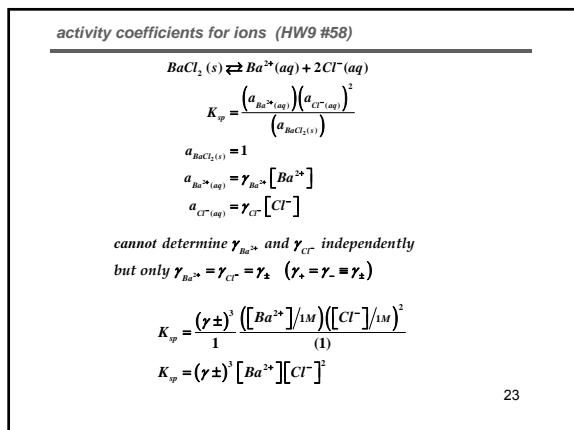
Debye-Hückel Theory

• 'a priori' calculation of activity coefficients, $\gamma_\pm$, for ions
• expect $\gamma_\pm < 1$ since ions not independent [effective concentration reduced; $a_\pm < c_\pm$]
• μ is calculated as work done to bring other charges to region surrounding ion in question
• the result is

$$\ln\gamma\pm = -\Omega\left|z_+z_-\right|T^{-\frac{3}{2}}I^{\frac{1}{2}}$$

where Ω depends on the solvent's dieelectric constant and other physical constants
z_+ and z_- are the (interger) charges on the cation and anion

and $I = \frac{1}{2}\sum_i m_i z_i^2$ is the ionic strength of the solution, m_i is molal concentration of *ion*

[E & R : Eqn 10.32 with κ from Eqn. 10.29]

24

4

Chemistry 163B
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Debye-Hückel Theory

$$\ln \gamma \pm = -\Omega |z_+ z_-| T^{-\frac{3}{2}} I^{\frac{1}{2}}$$

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[*E & R* : Eqn 10.32 with κ from Eqn. 10.29]

$$\log \gamma_\pm = -0.5092 |z_+ z_-| I^{\frac{1}{2}} \text{ for water solvent at 298.15K}$$

$$\ln \gamma_\pm = -1.173 |z_+ z_-| I^{\frac{1}{2}} \quad \text{(E\&R eqn 10.33)}$$

$$I = \frac{1}{2}\sum_i \left(m_{i+} z_{i+}^2 + m_{i-} z_{i-}^2\right) \quad \underline{\text{ionic strength}}$$

25

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observations: thermo ≡ heat

- Count Rumford, 1799
- observed water turning into steam when canon barrel was bored
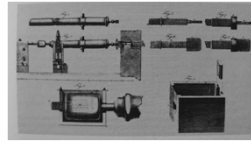- work ⇔ heat

FIGURE 11. An illustration from Rumford's paper, "An Inquiry Concerning the Source of the Heat Which is Excited by Friction," showing the apparatus used by him in the cannon boring experiment. Figure 1, upper left, shows the cannon as received from the foundry, and Figure 2, below, shows it mounted in the machine used for boring. (Reproduced with the permission of Harvard University Press.)

26

1ˢᵗ law
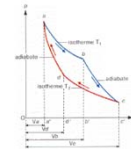
$$dU = \bar{d}q - PdV + dw_{other}$$

$$\oint dU = 0$$

$$dH = \bar{d}q + VdP + dw_{other}$$

27

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observations: mechanical efficiency of steam engine

- Sadi Carnot, 1824
- efficiency of engines

28

2ⁿᵈ Law

microstates and disorder

$$\varepsilon_{fficiency} \leq 1 - \frac{T_L}{T_H}$$

$$dS \geq \frac{\bar{d}q}{T}$$

$$dS = \frac{\bar{d}q_{rev}}{T}$$

$$\Delta S_{UNIVERSE} \geq 0$$

$$\oint dS = 0$$

$$dU = TdS - PdV + dw_{other}$$

$$dH = TdS + VdP + dw_{other}$$

29

"Applications"

How does knowledge about efficiencies of steam engines, mechanical systems, etc, relate to processes in chemical, biological, and geological systems?

ANSWERED BY:

J. W. Gibbs- arguably the frist great American scientist who combined the concepts of heat and entropy and proposed "[Gibbs] Free Energy", **G**, a thermodynamic state function that leads to a whole spectrum of applications

30

Free Energy and Equilibrium

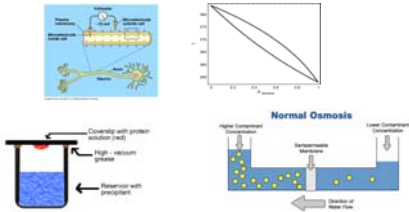$$\Delta G_{T,P} = \Delta H_{T,P} - T\Delta S_{T,P}$$

$$\frac{\Delta G_{T,P}}{T} = \underbrace{\frac{\Delta H_{T,P}}{T}}_{-\Delta S_{surroundings}} \underbrace{-\Delta S_{T,P}}_{-\Delta S_{system}}$$

$$dG = -SdT + VdP + dw_{other}$$

$$dA = -SdT - PdV + dw_{other}$$

31

Applications

32

quantitative-deductive mathematical abilities

$$dH = TdS + VdP + \sum_i \left(\frac{\partial H}{\partial n_i}\right)_{T,P,n_j \neq n_i} dn_i$$

Maxwell-Euler $\left(\frac{\partial V}{\partial S}\right)_{P,n_{all}} = \left(\frac{\partial T}{\partial P}\right)_{S,n_{all}}$

$$\left(\frac{\partial (\mu/T)}{\partial T}\right)_P = -\frac{\bar{H}}{T^2}$$

$$\left(\frac{\partial (\Delta\mu_{reac}/T)}{\partial T}\right)_P = -\frac{\Delta H_{reac}}{T^2}$$

$$\left(\frac{\partial \ln K_{eq}}{\partial T}\right)_P = \frac{\Delta H^o_{reac}}{RT^2}$$

33

Final Exam

- Conceptual and 'analytical math' from throughout term
- Problems concentrate on material since last exam
  - Ideal Solutions and corrections for non-ideality
  - Phase equilibria and phase diagrams
    one-component, relationship of T and P for one component equilibrium
    two-component (solid ⇌ solution and solution ⇌ vapor)
  - Colligative properties (**HW9**)
  - Electrochemistry (**HW9**)
    - Φ and ΔG, Δμ
    - Three cells
  - Vocabulary from concluding factoids
- **BRAIN POWER**

34

Chemistry 163B
Winter 2014
help sessions
Finals Prep

35

the lifetime warranty

36

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the warranty

From: Gene Switkes <gene@chemistry.ucsc.edu>
To: switkes@chemistry.ucsc.edu; XXXXXXXXX
Sent: Mon, February 15, 2010 10:51:17 AM
Subject: Re: **Question from former student**

Hi David,

Good to hear from you.
1983-- **don't know if the chem 101 warranty is still valid**
[just joking].

[answered question about disorder]

>Eugene Switkes,

37

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chem 163B warranty

Date: Mon, 15 Feb 2010 11:48:07 -0800 (PST)

From: David XXXX XXXXXXXXXXX

Subject: Re: Question from former student

Very helpful, thanks.

By the way, I had 163 with you, not 101... and I distinctly recall that you said that the 163 warranty **NEVER** expires...

Cheers, David

38

FINIS
(except)

39