

Chemistry 163B

Lecture 26- Concluding Factoids W2014

Lecture 26 Chemistry 163B Winter 2020

Concluding Factoids

and

Comments

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neuron, resting potential

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<http://projects.gw.utwente.nl/pisim/Bov/concep4.gif>

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

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resting potential and Nernst Equation

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

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 ²⁺)	0.1 μM	2 mM

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

$$\Phi^* = 0$$

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

$$\Phi = -\frac{RT}{n\mathcal{F}} \ln Q = -0.02569 \ln \frac{[K^+]_{inside}}{[K^+]_{outside}}$$

$$= -0.02569 \ln \frac{140 \text{ mM}}{5 \text{ mM}} = -0.086 \text{ V}$$

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

$$E_{rev} = \frac{RT}{zF} \ln \left[\frac{P_K [K^+]_o + P_{Na} [Na^+]_o + P_{Cl} [Cl^-]_i}{P_K [K^+]_i + P_{Na} [Na^+]_i + P_{Cl} [Cl^-]_o} \right]$$

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vocabulary

Gibbs-Duhem

the partial molar quantities do not vary independently

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Gibbs-Duhem

what are $\left(\frac{\partial \bar{V}}{\partial n_i}\right)_{T,P,n_j}$ and $\left(\frac{\partial \bar{V}}{\partial n_i}\right)_{T,P,n_j}$ 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

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non-ideal solutions

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

Raoult's Law of Ideal Solutions

$$P_A = X_A^{(l)} P_A^* \quad P_B = X_B^{(l)} P_B^*$$

$$P_{total} = X_A^{(l)} (P_A^* - P_B^*) + P_B^*$$

Benzene and Toluene

http://www.chem.ucsb.edu/courses/pages/06fall11C-Walsh/01Lecture_Notes/Lecture16.%2011-8-06Colligative%20Properties%20Solutions.pdf

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

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
 $X_i^{(l)} = X_i^{(v)}$
- boiling point of azeotrope may be higher or lower than of pure liquids

non-ideal solutions: positive deviations from ideal solution (E&R, pp252-254 214-218, ...)

CS₂ (l) + (CH₃)₂CO (l)

Figure 9-13 Deviations from Raoult's law. The data in Table 9-3 are plotted versus X_{CS₂}. Dashed lines show the expected behavior if Raoult's law were obeyed

- positive deviations from Raoult's Law: smaller forces between components than 'within' components
- total pressure greater than ideal solution

acetone-carbon disulfide: positive deviation ⇒ low boiling azeotrope

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

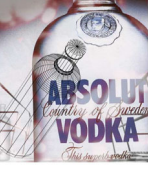
low boiling azeotrope

- 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

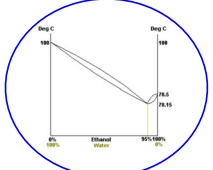
http://www.solvent-recycling.com/azeotrope_1.html


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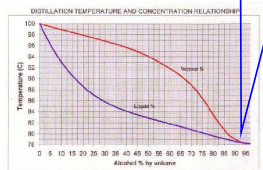


Water-Ethanol Mixture





DISTILLATION TEMPERATURE AND CONCENTRATION RELATIONSHIP



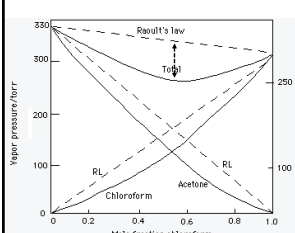
Temperature (C) vs Alcohol % by volume

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.

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non-ideal solutions : **negative deviations** from ideal solution

$\text{CHCl}_3(l) + (\text{CH}_3)_2\text{CO}(l)$

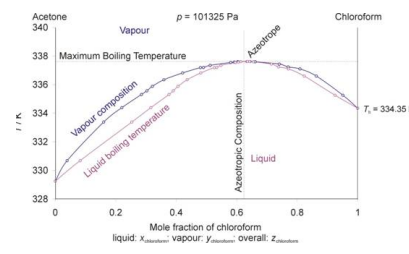


Vapor pressure/torr vs Mole fraction chloroform

- **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**



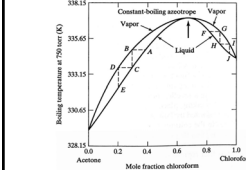
Maximum Boiling Temperature, Azeotropic Composition, Vapour composition, Liquid boiling temperature, Mole fraction of chloroform

$$\begin{matrix} & \text{H}_3\text{C} & & & \\ & | & & & \\ \text{H}_3\text{C} & -\text{C} & =\text{O} & \cdots & \text{H} & -\text{Cl}_3 \\ & | & & & & \\ & \text{H}_3\text{C} & & & & \end{matrix}$$

Figure 9-8 Hydrogen bond formation between acetone and chloroform. The relatively strong bonding between species leads to the formation of a maximum boiling azeotrope

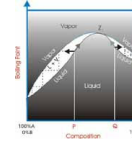
http://www.chm.bris.ac.uk/~chdms/Teaching/Chemical_Interactions/images/pic192.jpg 15

high boiling azeotrope



Boiling temperature at 20 torr (K) vs Mole fraction chloroform

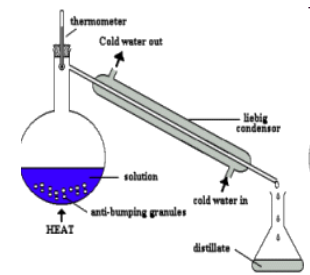
- stronger between component forces (A↔B) (than A ↔A, B ↔B)
- fractional distillation leads to pure component in vapor until solution (pot) reaches azeotrope composition
- $(X_A)_{\text{initial}} > (X_A)_{\text{azeotrope}}$ pure A
- $(X_A)_{\text{initial}} < (X_A)_{\text{azeotrope}}$ pure B



Composition

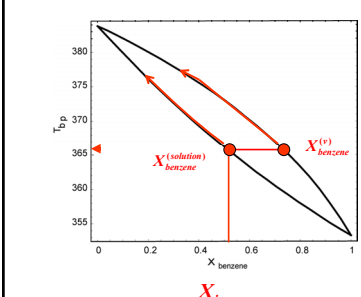
http://www.solvent-recycling.com/azeotrope_1.html 16

simple distillation



http://www.docbrown.info/page12/gifs/distill.gif 17

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



T_{bp} vs X_{benzene}

add heat

$X_{\text{benzene}}^{(\text{solution})}$ decreases

T_{bp} increases gradually

$X_{\text{benzene}}^{(\text{solution})}$ $X_{\text{benzene}}^{(\text{v})}$

X_{benzene} X_{benzene}

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fractional distillation

<http://www.wpbschoolhouse.blinternet.co.uk/page12/gifs/FracDistRed.gif>

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Fractional Distillation

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

II. • vapor $X_{benzene}^v \approx .72$

III. • condense $X_{benzene}^v \approx .72$
• $T_{bp} \approx 359.5$

IV. • evaporate
• vapor $X_{benzene}^v \approx .88$

V. etc, ...

VI. approaches
 $X_{benzene} = 1$ 20

T vs progress for a distillation

<http://www.uwfax.edu/faculty/koster/Image119.gif>

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**Electrolytes and
Debye-Huckel Theory**

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activity coefficients for ions (HW8 #58)

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

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

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

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

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

cannot determine $\gamma_{Ba^{2+}}$ and γ_{Cl^-} independently
but only $\gamma_{Ba^{2+}} = \gamma_{Cl^-} = \gamma_{\pm}$ ($\gamma_+ = \gamma_- = \gamma_{\pm}$)

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

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

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Debye-Hückel Theory

- 'a priori' calculation of activity coefficients, γ_{\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

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

where Ω depends on the solvent's dielectric constant and other physical constants
 z_+ and z_- are the (integer) charges on the cation and anion
and $I = \frac{1}{2} \sum m_i z_i^2$ is the ionic strength of the solution, m_i is molal concentration of ion
[E & R₁₀: Eqn 10.32 with κ from Eqn. 10.29]

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Debye-Hückel Theory

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

where Ω depends on the solvent's dielectric constant and other physical constants
 z_+ and z_- are the (integer) charges on the cation and anion
 and $I = \frac{1}{2} \sum m_i z_i^2$ 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]

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

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

$I = \frac{1}{2} \sum (m_{+} z_{+}^2 + m_{-} z_{-}^2)$ ionic strength

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from cumulative review

- Concluding factoids
 - Thermodynamics is useful whole quarter !!
 - Electrical potential across membranes (e.g. neurons) can be calculated using Nernst equation slides 2-3
 - Non-idealities in solutions
 - Azeotropes and eutectics: constant boiling and melting solutions slides 6-21
 - Negative deviation from Raoult's Law (stronger forces; high boiling azeotrope) slides 14-16
 - Positive deviation from Raoult's Law (weaker forces; low boiling azeotrope) slides 10-13
 - Gibbs-Duhem: slides 4-5 partial molar properties for differing components are interdependent
 - Debye-Huckel slides 22-25 Theoretical method for calculating γ_{\pm} for electrolytes (note $\gamma_{\pm} \leq 1$)

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observations: thermo \equiv heat

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

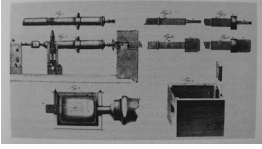
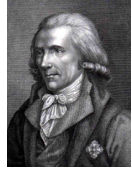




FIGURE 11. An illustration from Rumford's paper, "An Inquiry Concerning the Source of the Heat Which is Excited by Friction," showing the apparatus used by him in the cannon boring experiment. Figure 1, upper left, shows the cannon as received from the foundry, and Figure 2, below, shows it mounted in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

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1st law

$$dU = \delta q - PdV + dw_{other}$$


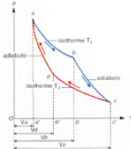

$$\oint dU = 0$$

$$dH = \delta q + VdP + dw_{other}$$


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observations: mechanical efficiency of steam engine

- Sadi Carnot, 1824
- efficiency of engines

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2nd Law

~~microstates and disorder~~

$$\epsilon_{efficiency} \leq 1 - \frac{T_L}{T_H}$$


$$dS \geq \frac{\delta q}{T}$$

$$dS = \frac{\delta q_{rev}}{T}$$

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

$$\oint dS = 0$$

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

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


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"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 first 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


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Free Energy and Equilibrium

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

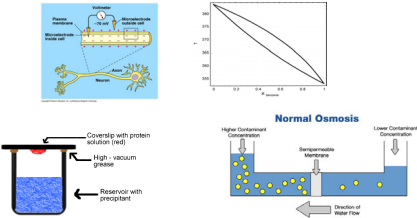
$$\frac{\Delta G_{T,P}}{T} = \frac{\Delta H_{T,P}}{T} - \frac{-\Delta S_{T,P}}{-\Delta S_{\text{surroundings}} - \Delta S_{\text{system}}}$$

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

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


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Applications



Normal Osmosis

Higher Concentration | Semipermeable Membrane | Lower Concentration

Direction of Water flow

Control pip with protein solution (10%)
High vacuum grease
Reservoir with precipitant

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quantitative-deductive mathematical abilities

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

Maxwell-Euler

$$\left(\frac{\partial V}{\partial S} \right)_{P,n_{i,j}} = \left(\frac{\partial T}{\partial P} \right)_{S,n_{i,j}}$$

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

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

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

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Final Exam

- Conceptual and 'analytical math' from throughout term
- Problems concentrate on material since last exam
 - Partial molar quantities, $\Delta\mu$ for variable composition
 - 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 \rightleftharpoons solution and solution \rightleftharpoons vapor)
- Colligative properties (**HW8**)
- Electrochemistry (**HW8**)
 - Φ and ΔG , $\Delta\mu$
 - Three cells
- Vocabulary from concluding factoids

BRAIN POWER

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FINALS PREP HELP SCHEDULE CHEMISTRY 163B

Week of March 17-20

Friday, 14 March	9:00-10:00 AM 11:00-12:30 AM 2:00-3:00 PM	1667187 P&S CL1 E&S S&S	Regular Office Hours Scribes Regular Lecture Lecture/Discussion Regular Discussion Medick
Sunday, 15 March	• Sample Final Key on eComments		
Monday, 17 March	11:00-12:30 AM 2:00-3:00 PM	1667187 P&S CL1	S&S Scribes Lecture/Discussion Regular Office Hours Scribes
Tuesday, 18 March	4:00-5:00 PM	146 P&S	L&P Office Review Office Hours
Wednesday, 19 March	10:00-12:00 AM	141 P&S	L&P Office Review Office Hours Medick
Thursday, 20 March	FINAL EXAM 12:00-3:00 PM Classroom 1		

Chemistry 163B
Winter 2020
help sessions
Finals Prep

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FINIS
(except)

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**MUCH
Thanks To
two GREAT TAs**

Evan and Pam



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Some Important Points for Chemistry 163B On-Line Final

Get Ready for 19th March 4-7 PM

- Be prepared to have a reliable internet connection to CANVAS
- Have plenty of scratch paper handy (the exam will not be accepting 'show work'; only final solutions)
- You may want to have printed out the "Relationships for Final" set of formulas for use on on-line exam. See below for other materials that you may (and may not) use
- On Monday, 18th March, DANA (DPM) will make CANVAS final notes available for you. Here I have taken a couple of questions from the "Sample Final Exam" (old fashion pdf on CANVAS, available now, RTY on 15th March) and converted them to how our on-line final will look. Please SUBMIT your responses of Evan, Pam, Inrah, and I can shake out our "hand grading" protocol. YOU 'SCORE' ON THIS TRIAL EXAM IS NOT A PART OF YOUR CLASS GRADE.

FOR THE EXAM 19th March 4-7 PM

- Be at a place where you have a reliable internet connection to CANVAS
- The exam is
 - "open book" (you may use) for
 - anything on [class WWW site](#)
 - anything on our student accessible [class CANVAS SITE](#)
 - "closed book" you may NOT USE
 - any books (e.g. textbook)
 - CLASS lecture WEBCASTS
 - any other material on the WWW
- Points for problems indicating "marked by hand" will be scored by exam readers later in the week and added to the exam total
- If you start on time, you will have the allotted 3 hours (DRC additional) but the exam will disappear at 7PM (DRC additional)
- However, don't be surprised if you only need 60-90 minutes to complete the exam

take care

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