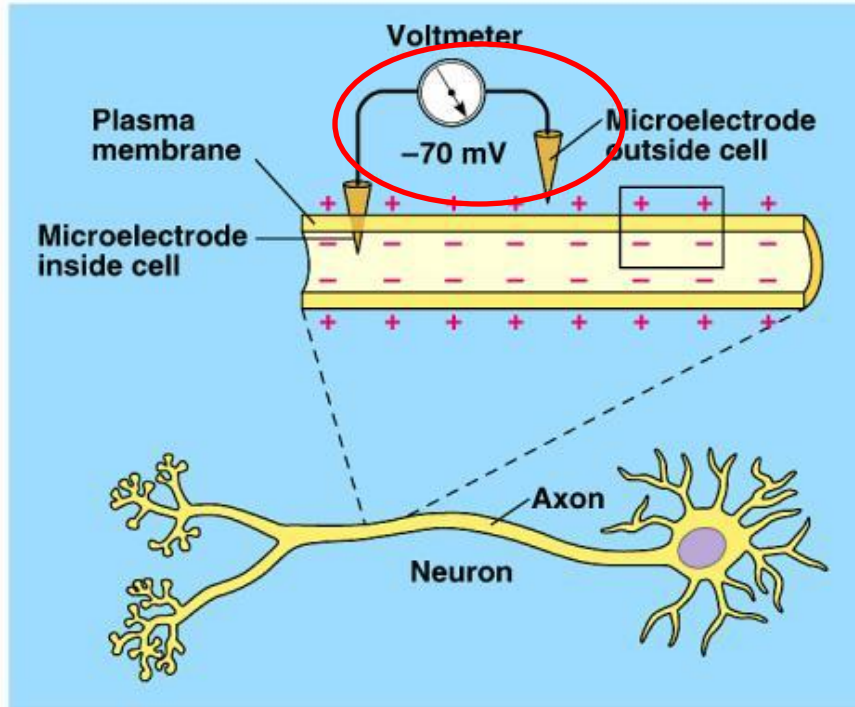
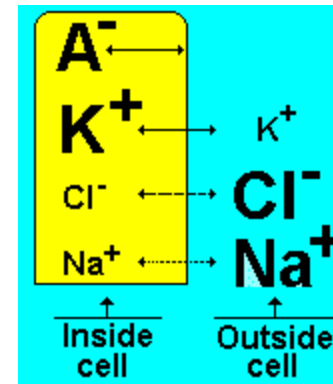
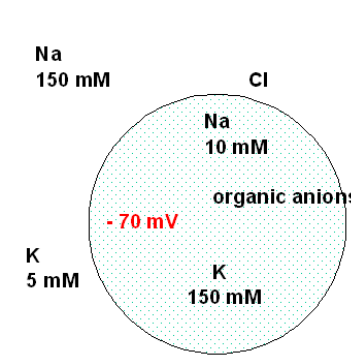


Chemistry 163B
Concluding Factoids
and
Comments

neuron, resting potential



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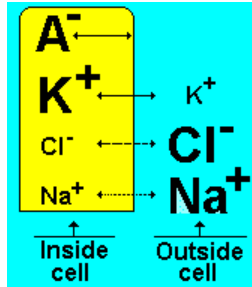


<http://projects.gw.utwente.nl/pi/sim/Bovt/concep4.gif>

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

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^{++})	0.1 μ M	2 mM

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

$$\Phi^\circ = 0$$

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

$$\begin{aligned} \Phi &= -\frac{RT}{n\mathcal{F}} \ln Q = -.02569 \ln \frac{[K^+]_{inside}}{[K^+]_{outside}} \\ &= -.02569 \ln \frac{140 \text{ mM}}{5 \text{ mM}} = -0.086 \text{ V} \end{aligned}$$

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

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

Gibbs-Duhem

the partial molar quantities do not vary independently

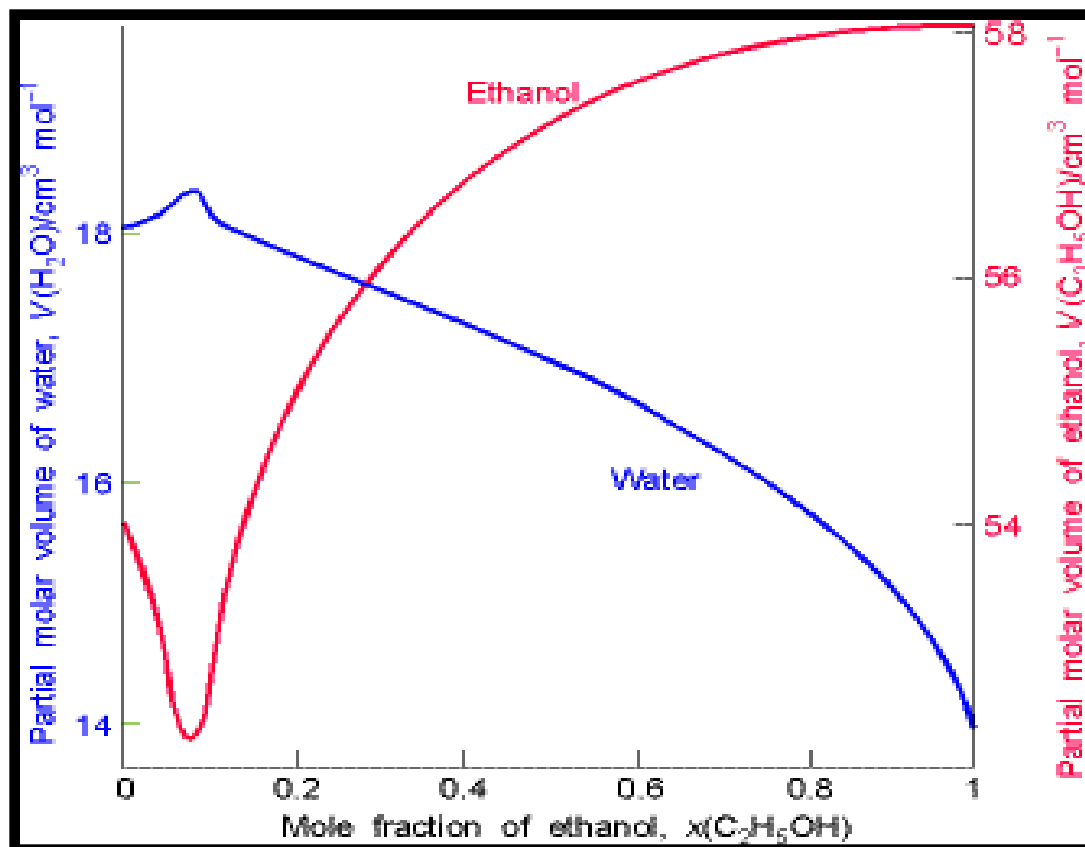
Gibbs-Duhem

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

what are

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

when a and b
form an ideal solution ?



do ideal
solutions
obey the
Gibbs-Duhem
relation?



non-ideal solutions

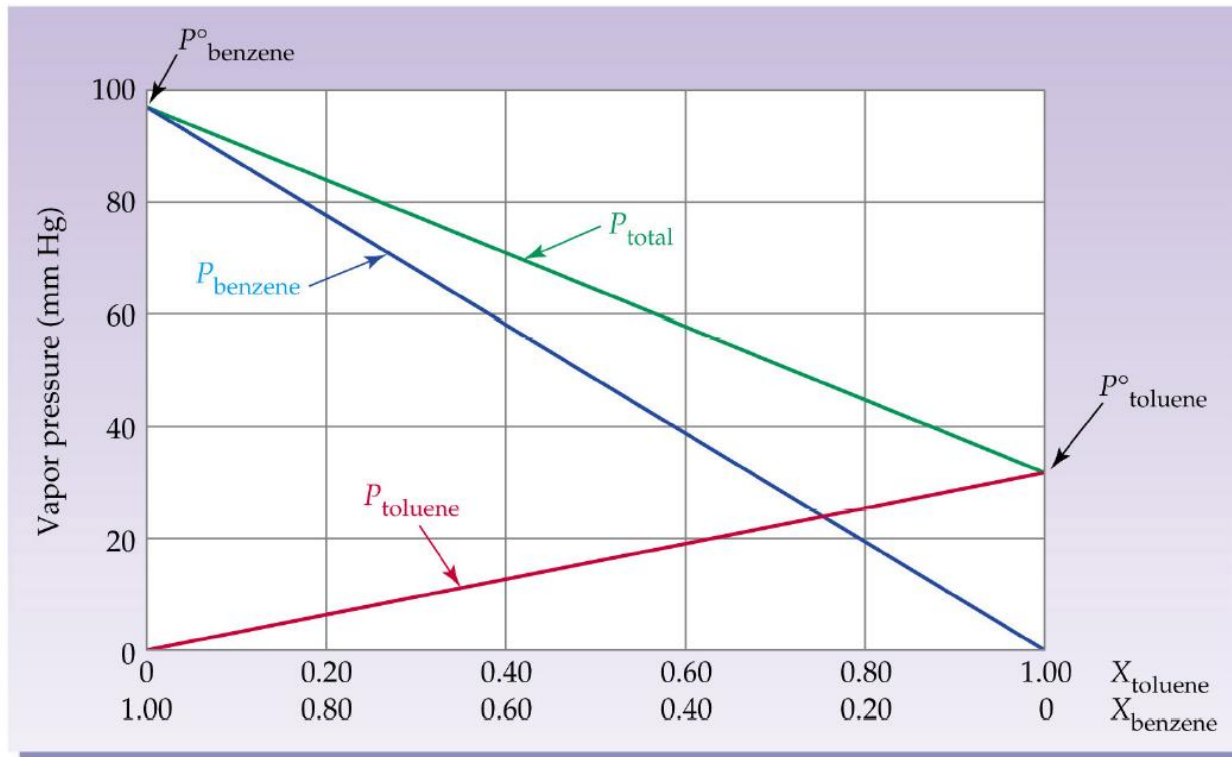
benzene-toluene, quite ideal (similar to Fig 9.2 E&R) !!

Raoult's Law of Ideal Solutions

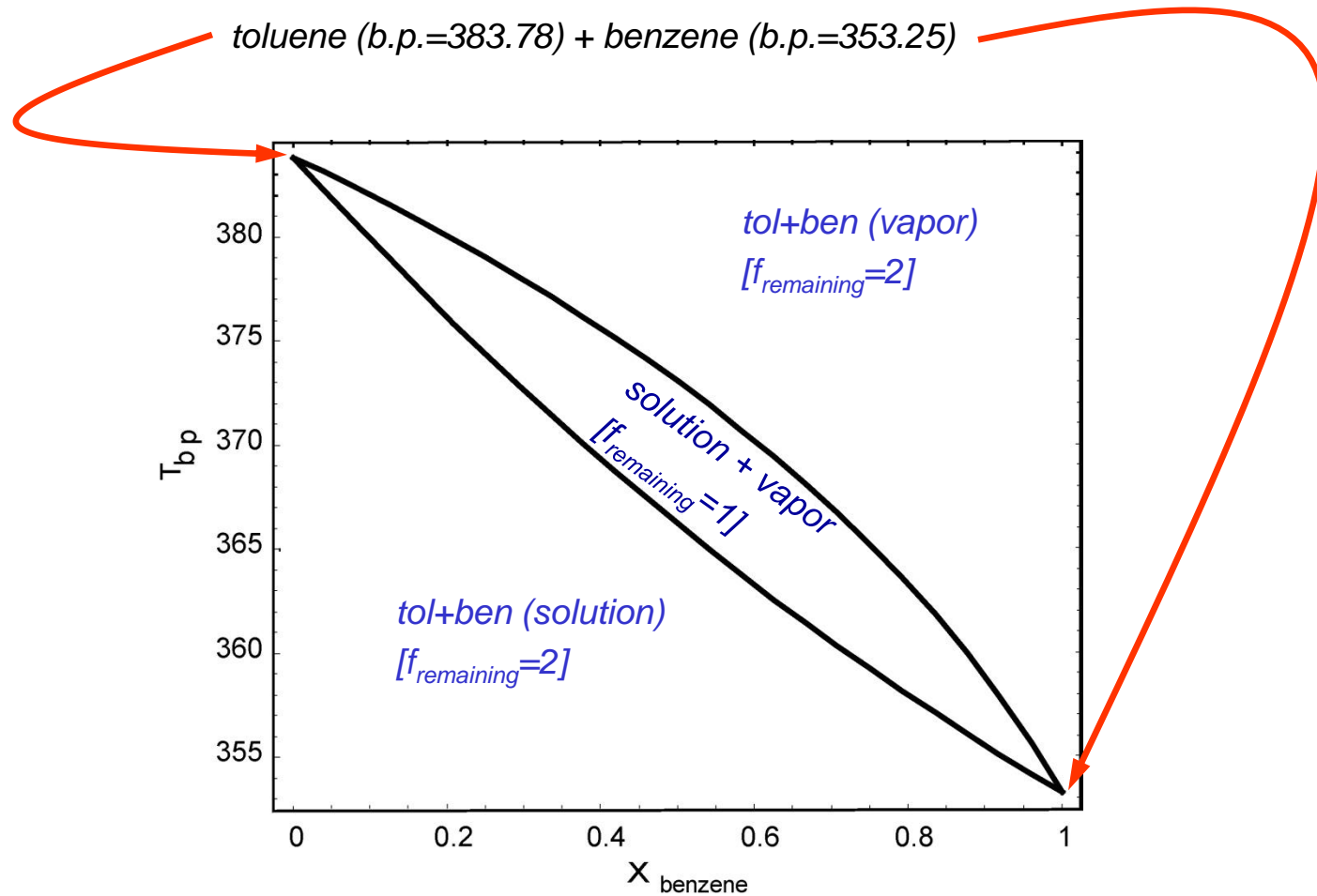
$$P_A = X_A^{(\ell)} P_A^\bullet \quad P_B = X_B^{(\ell)} P_B^\bullet$$

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

Benzene and Toluene



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



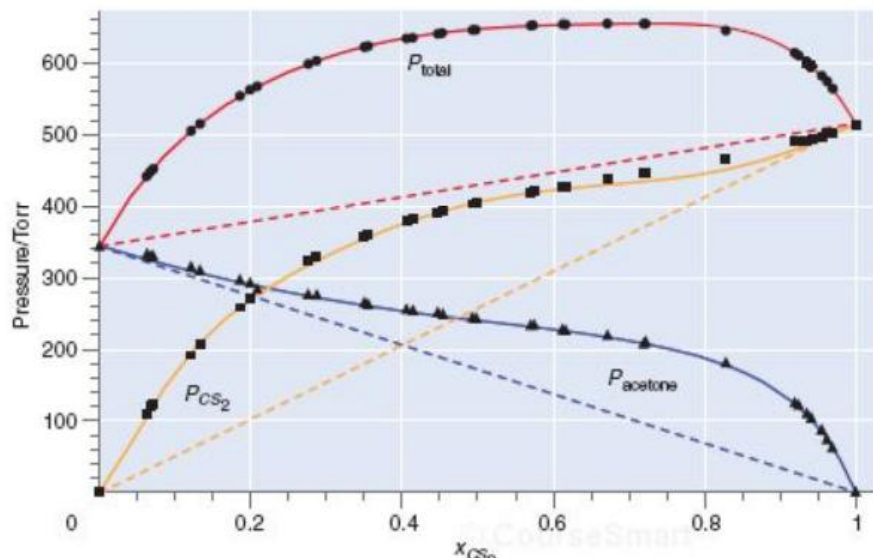
non-ideal solutions: azeotrope

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

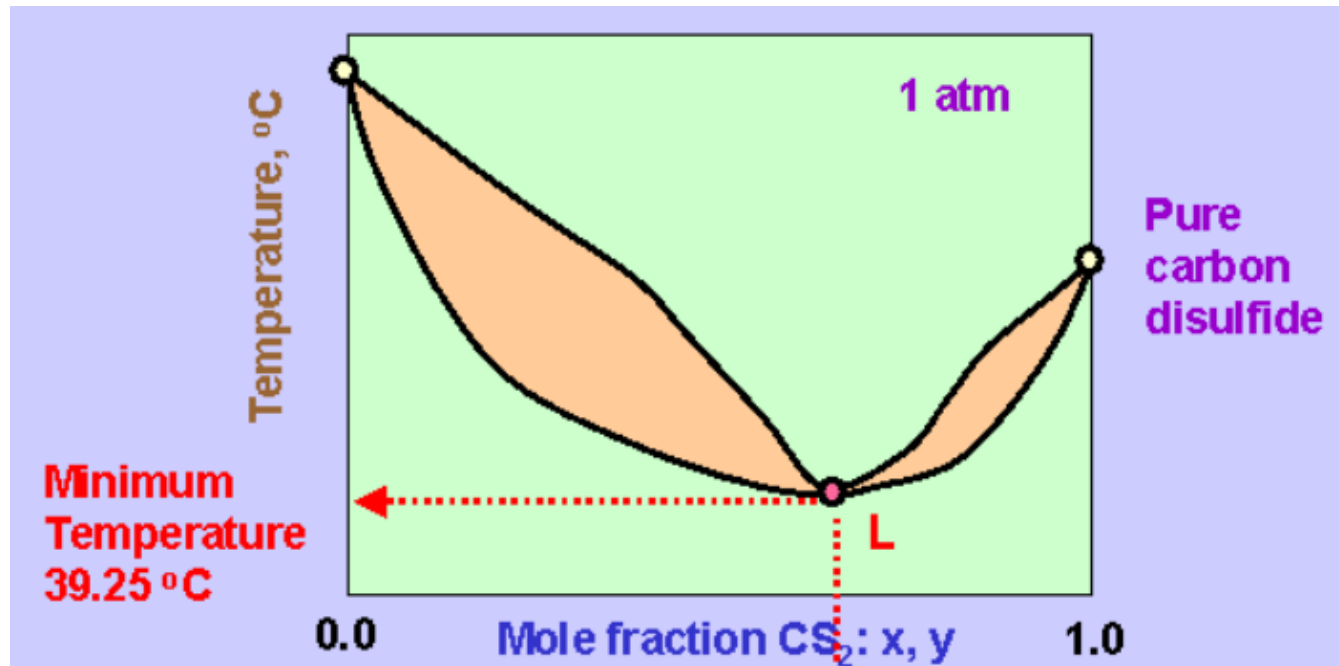


- positive deviations from Raoult's Law: smaller forces between components than 'within' components
- total pressure greater than ideal solution

FIGURE 9.13

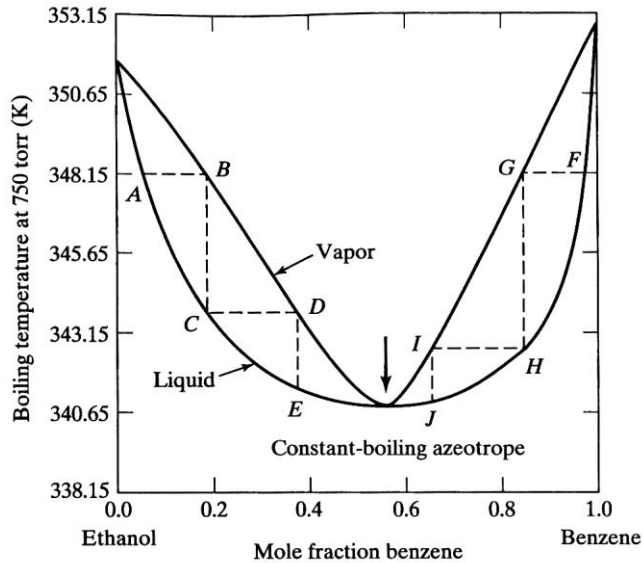
The data in Table 9.3 are plotted versus x_{CS_2} . The dashed lines show the expected behavior if Raoult's law were obeyed.

acetone-carbon disulfide: positive deviation \Rightarrow low boiling azeotrope

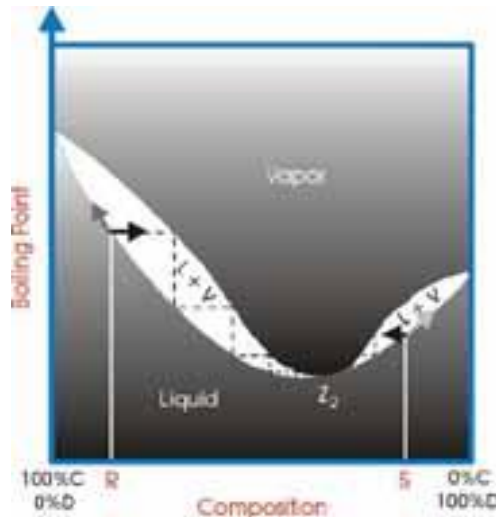


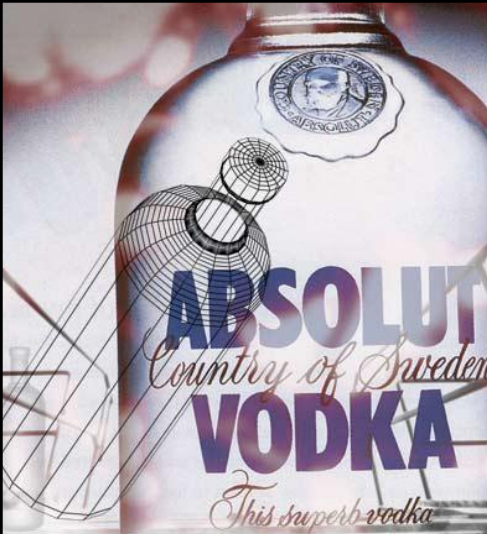
<http://www.separationprocesses.com/Distillation/Fig011b.htm>

low boiling azeotrope

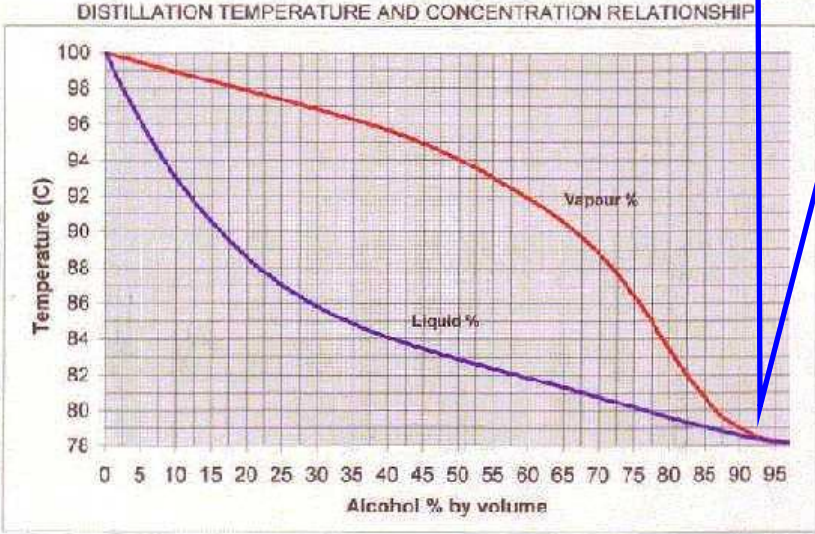
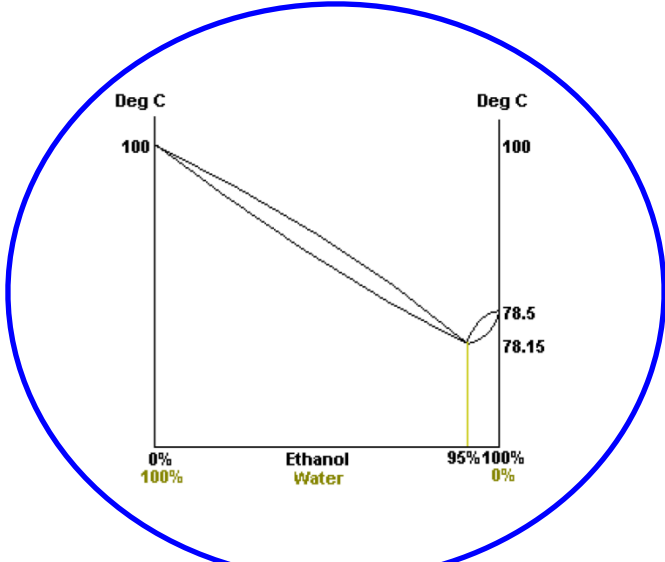


- weaker between component forces ($A \leftrightarrow B$) (than $A \leftrightarrow A$, $B \leftrightarrow B$)
- fractional distillation leads to constant boiling azeotrope in vapor
- and (in **pot** after azeotrope boils off)
 - $(X_A)_{\text{initial}} > (X_A)_{\text{azeotrope}}$ pure A
 - $(X_A)_{\text{initial}} < (X_A)_{\text{azeotrope}}$ pure B



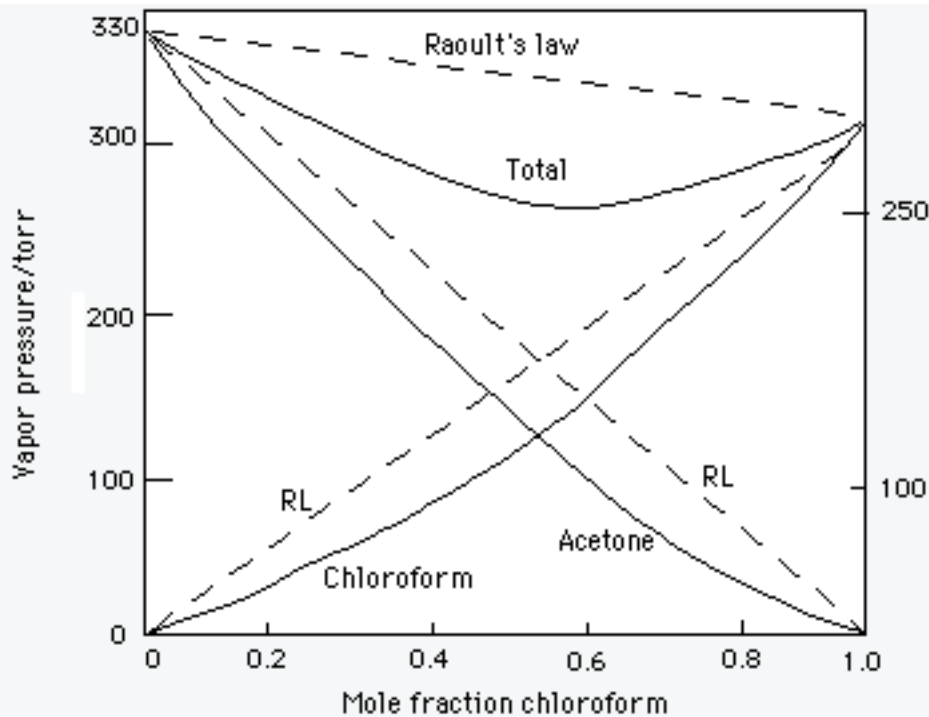
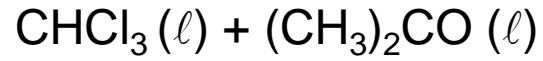


Water-Ethanol Mixture



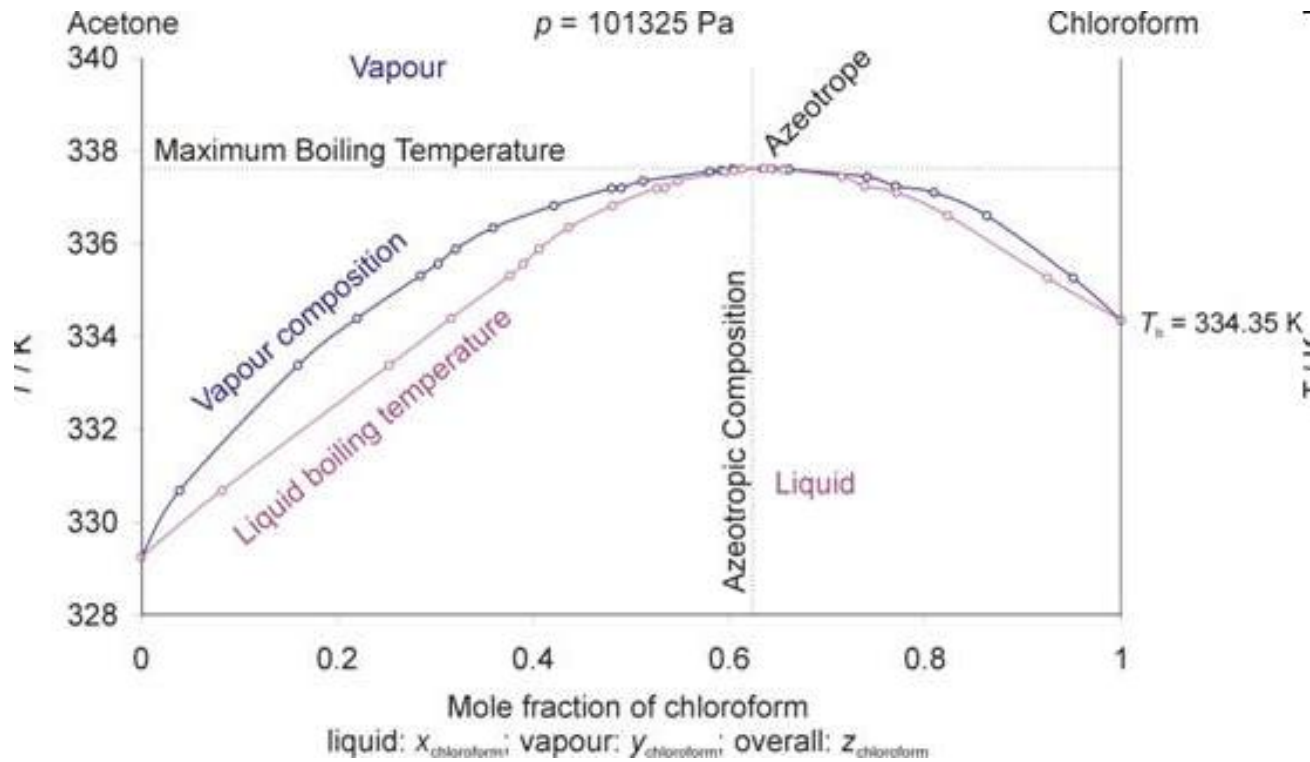
For the water-ethanol mixture, the azeotrope concentration corresponds to ~95% of ethanol in the mixture. This is the limit that can be reached by distillation of a less-alcohol-rich mixture.

non-ideal solutions : negative deviations from ideal solution



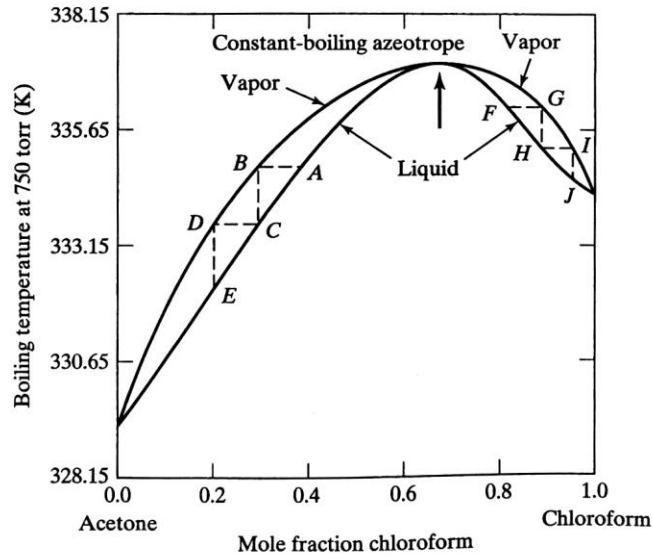
- **negative deviations from Raoult's Law: greater forces between components than 'within' components**
- **total pressure lower than ideal solution**

acetone-chloroform: negative deviation \Rightarrow high boiling azeotrope



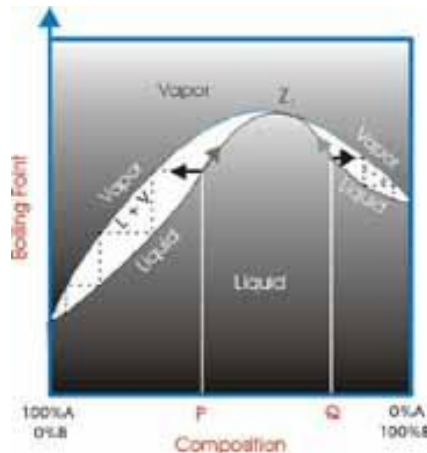
http://www.chm.bris.ac.uk/~chdms/Teaching/Chemical_Interactions/images/pic192.jpg

high boiling azeotrope

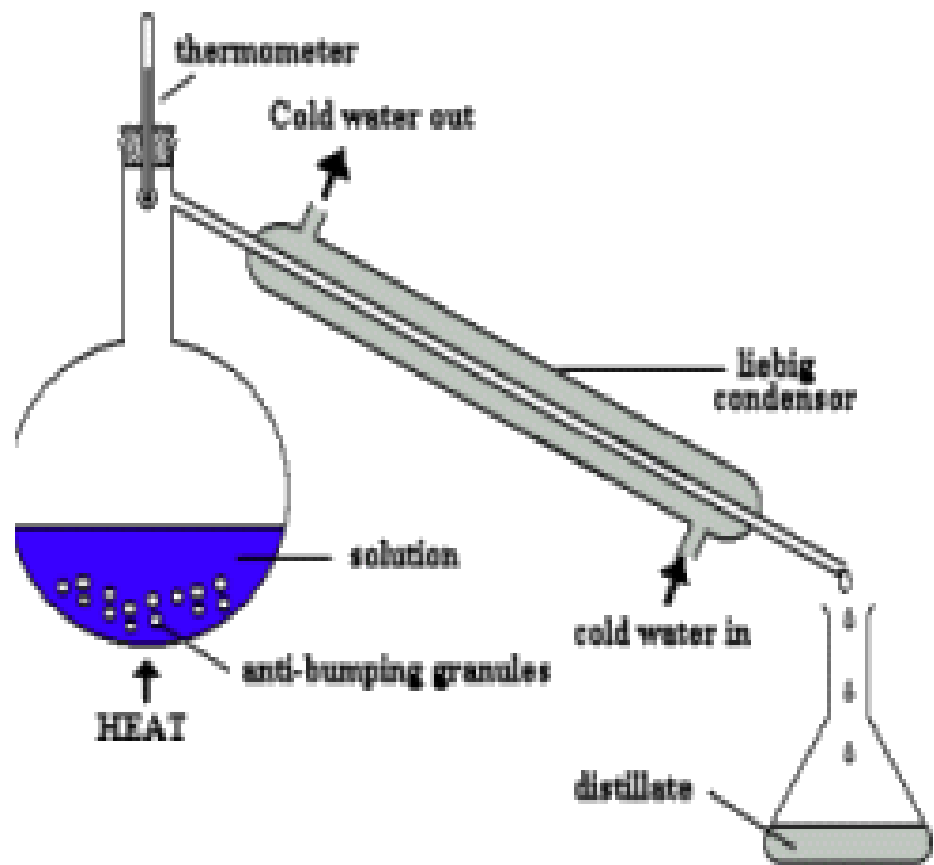


- stronger between component forces ($A \leftrightarrow B$) (than $A \leftrightarrow A$, $B \leftrightarrow B$)
- fractional distillation leads to pure component in vapor until solution (pot) reaches azeotrope composition

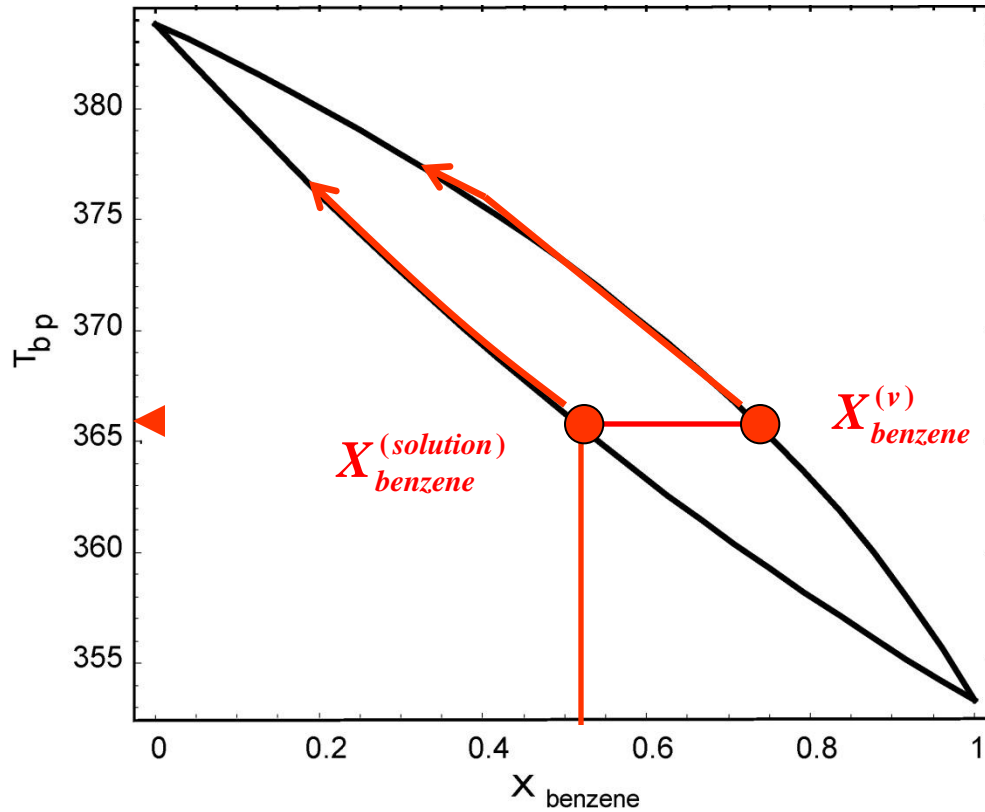
- $(X_A)_{\text{initial}} > (X_A)_{\text{azeotrope}}$ pure A
- $(X_A)_{\text{initial}} < (X_A)_{\text{azeotrope}}$ pure B



simple distillation



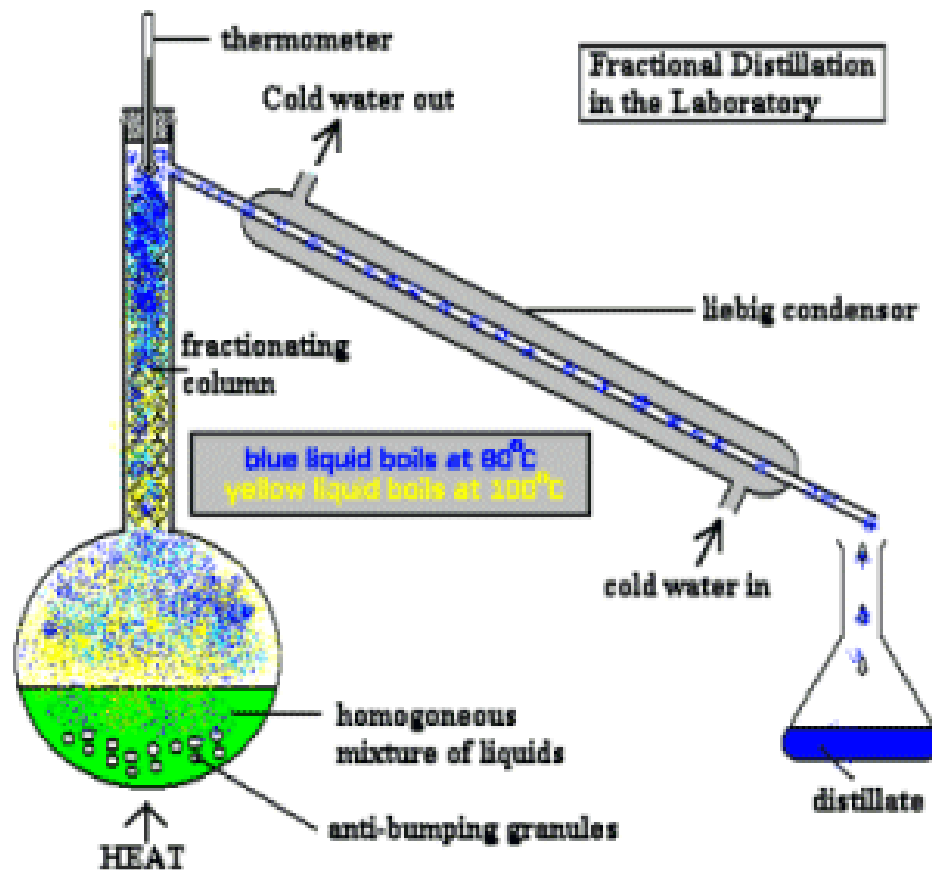
simple distillation (one evaporation; T_{bp} varies as X changes)



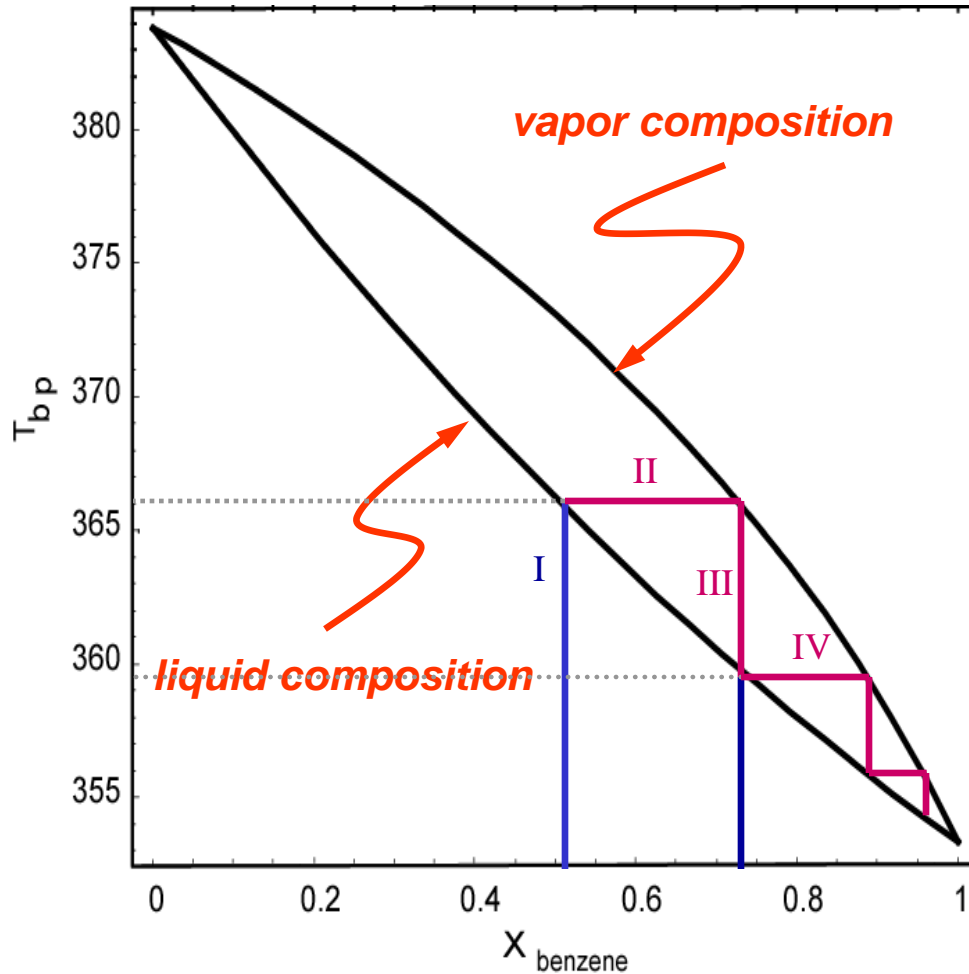
add heat
 $X_{benzene}^{(solution)}$ *decreases*
 T_{bp} *increases gradually*

$X_{benzene}$

fractional distillation



Fractional Distillation



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

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

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

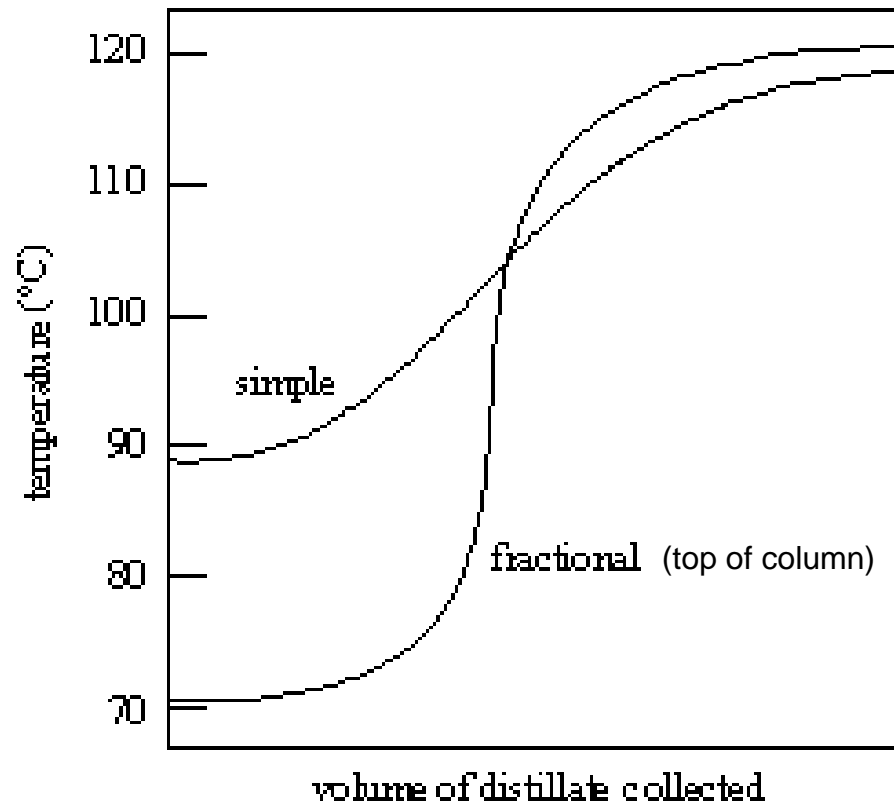
IV. • evaporate
• vapor $X_{benzene}^v \approx .88$

V. etc, ...

VI. approaches

$X_{benzene} = 1$ 20

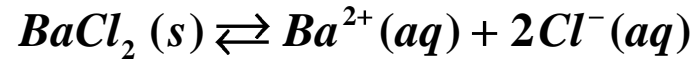
T vs progress for a distillation



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

Electrolytes and Debye-Huckel Theory

activity coefficients for ions (HW9 #58)



$$K_{sp} = \frac{a_{\text{Ba}^{2+}(aq)} a_{\text{Cl}^{-}(aq)}^2}{a_{\text{BaCl}_2(s)}}$$

$$a_{\text{BaCl}_2(s)} = 1$$

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

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

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

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

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

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

Debye-Hückel Theory

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

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

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 $I = \frac{1}{2} \sum_i m_i z_i^2$ 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]

Debye-Hückel Theory

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

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 $I = \frac{1}{2} \sum_i m_i z_i^2$ 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]

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

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

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

observations: *thermo* \equiv *heat*

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

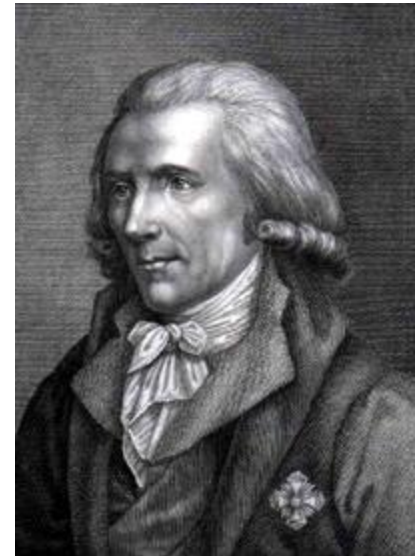
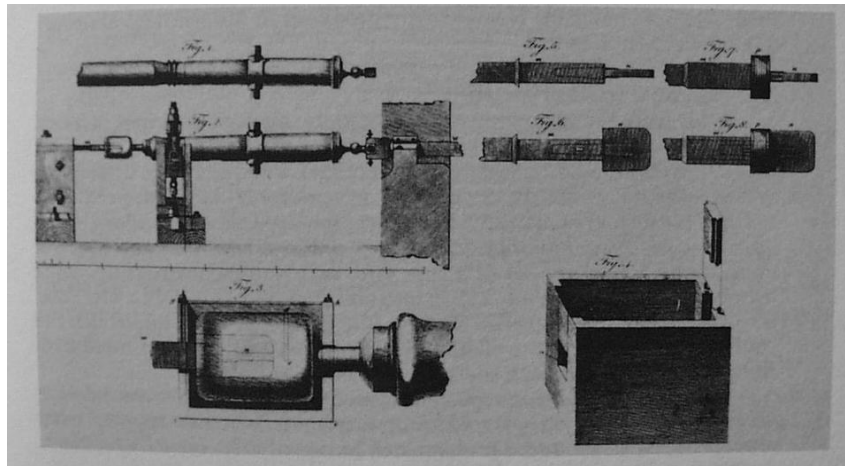
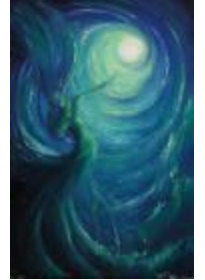


FIGURE 11. An illustration from Rumford's paper, "An Inquiry Concerning the Source of the Heat Which is Excited by Friction," showing the apparatus used by him in the cannon boring experiment. Figure 1, upper left, shows the cannon as received from the foundry, and Figure 2, below, shows it mounted in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



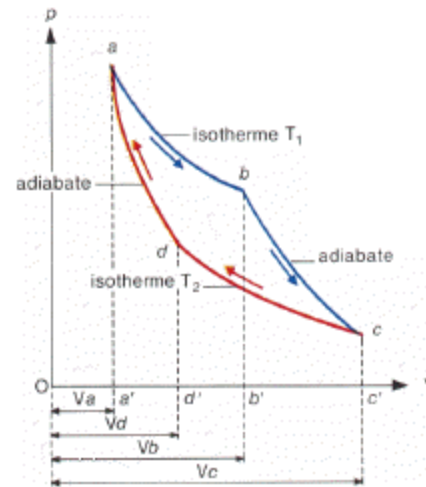
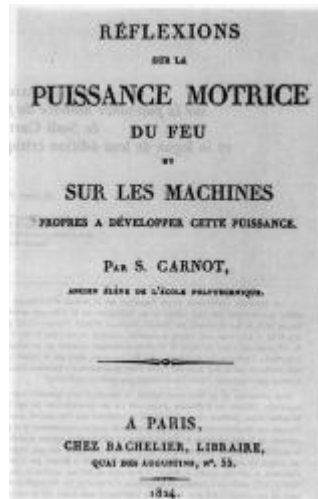
$$dU = \vec{d}q - PdV + dw_{other}$$

$$\oint dU = 0$$

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

observations: mechanical efficiency of steam engine

- Sadi Carnot, 1824
- efficiency of engines



microstates and disorder



$$\varepsilon_{\text{efficiency}} \leq 1 - \frac{T_L}{T_H}$$

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

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

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

$$\oint dS = 0$$

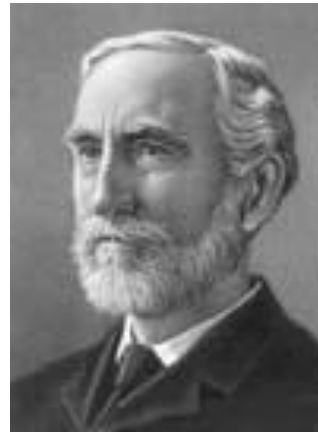
$$dU = TdS - PdV + dw_{\text{other}}$$

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

“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

Free Energy and Equilibrium



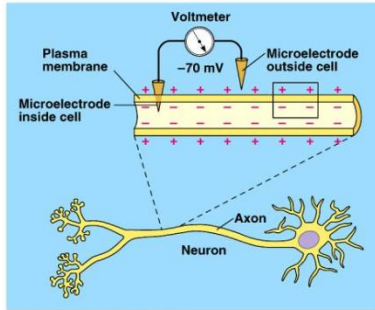
$$\Delta G_{T,P} = \Delta H_{T,P} - T \Delta S_{T,P}$$

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

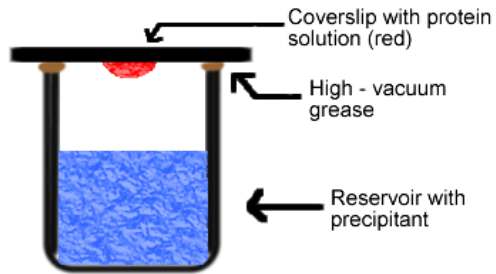
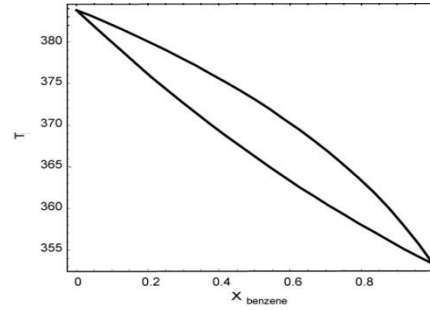
$$dG = -SdT + VdP + dw_{other}$$

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

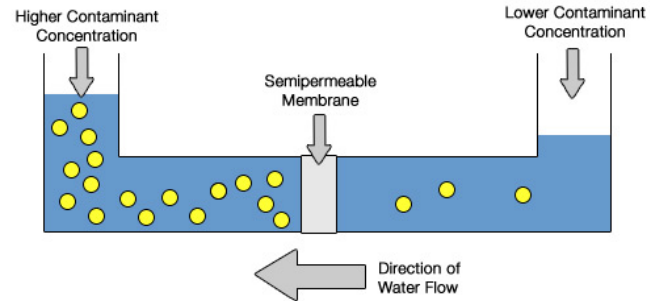
Applications



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Normal Osmosis



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

Maxwell-Euler

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

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

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

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

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 \rightleftharpoons solution and solution \rightleftharpoons vapor)
 - Colligative properties (**HW9**)
 - Electrochemistry (**HW9**)
 - Φ and ΔG , $\Delta\mu$
 - Three cells
 - Vocabulary from concluding factoids
- **BRAIN POWER**

FINALS PREP HELP SCHEDULE CHEMISTRY 163B

Week of March 17-20

Friday, 14 March	9:00-10:00 AM	1567/157 PSB	Regular Office Hours <i>Switkes</i>
	11:00-12:30 AM	CL1	Regular Lecture ELECTROCHEMISTRY II
	2:00-3:00 PM	E&MS B214	Regular Discussion <i>Mednick</i>
	<ul style="list-style-type: none"> • Sample Final on eCommons • HW#9 Solutions on eCommons • Review Weeks 8-10 on WWW 		
Sunday, 16 March	<ul style="list-style-type: none"> • Sample Final Key on eCommons 		
Monday, 17 March	11:00-12:30 AM	CL1	LAST Class <i>Switkes</i> CONCLUDING FACTOIDS
	2:00-3:00 PM	1567/157 PS	Regular Office Hours <i>Switkes</i>
	5:00-6:30 PM Thimann 1 Review Session <i>Switkes</i>		
Tuesday, 18 March	4:00-5:00 PM	145 PSB	Last Chance Review Office Hours <i>Liu</i>
Wednesday, 19 March	10:00-12:00 AM	341 PSB	Last Chance Review Office Hours <i>Mednick</i>
Thursday, 20 March	FINAL EXAM 12:00-3:00 PM Classroom 1		

Chemistry 163B
Winter 2014
help sessions
Finals Prep



the warranty

From: Gene Switkes <gene@chemistry.ucsc.edu>
To: switkes@chemistry.ucsc.edu; XXXXXXXXXXXX
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,

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

From: David XXXX XXXXXXXXXXXXX

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



FINIS

(except)