

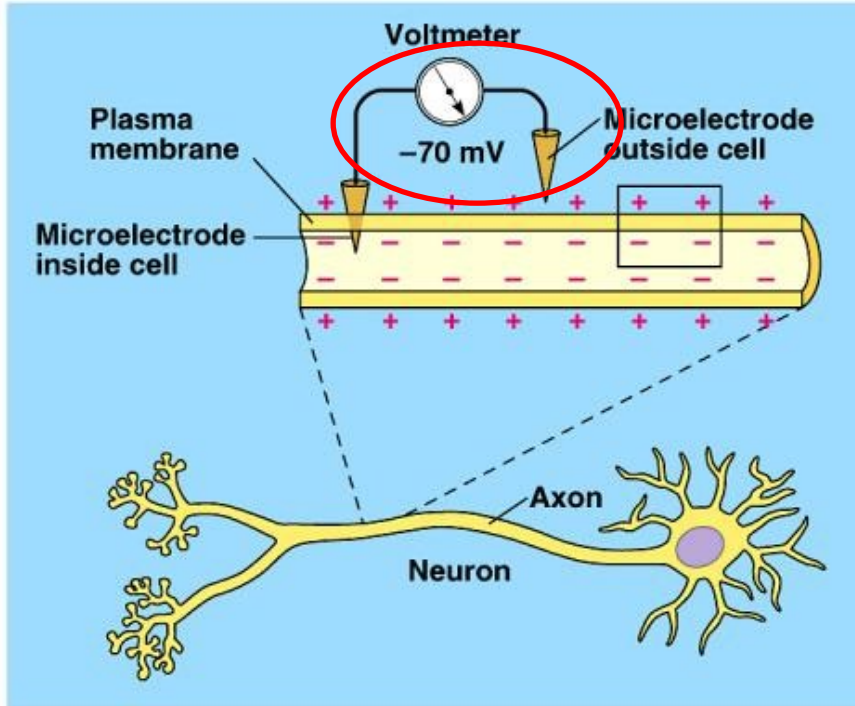
*Lecture 26 Chemistry 163B Winter 2020*

*Concluding Factoids*

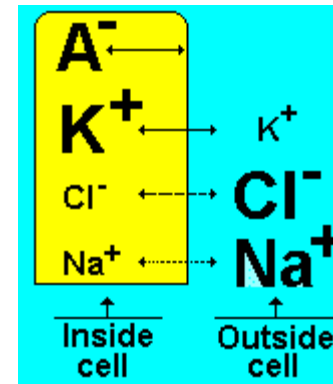
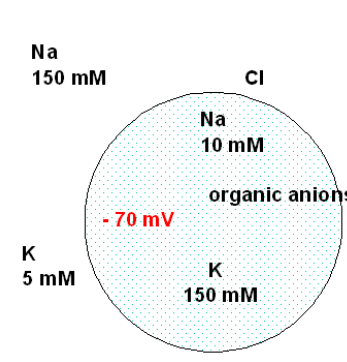
*and*

*Comments*

# neuron, resting potential



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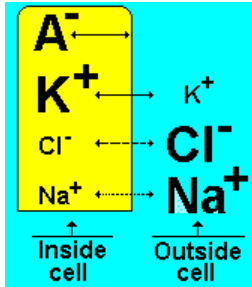


<http://projects.gw.utwente.nl/pi/sim/Bovt/concep4.gif>

[http://www.uta.edu/biology/westmoreland/classnotes/1442/Chapter\\_48\\_files/image009.jpg](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 $\mu$ M	2 mM

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

$$\Phi^\circ = 0$$

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

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

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

**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](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

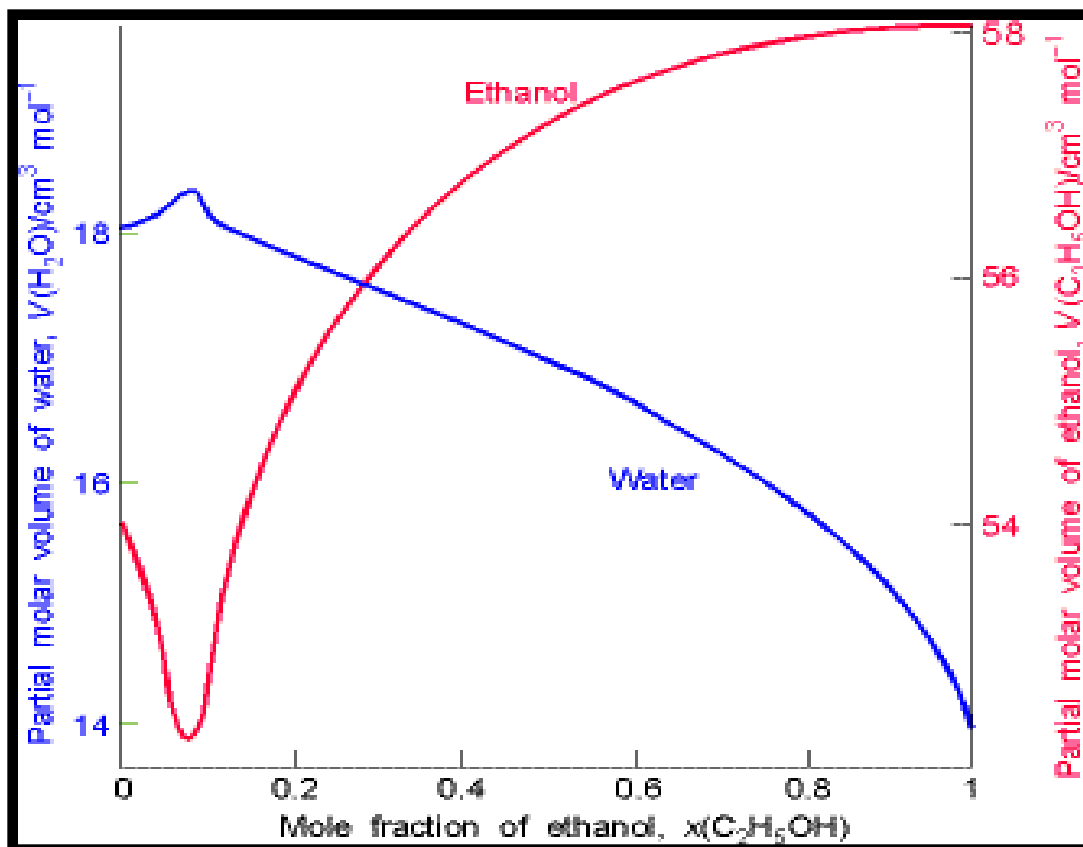
# Gibbs-Duhem

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

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**

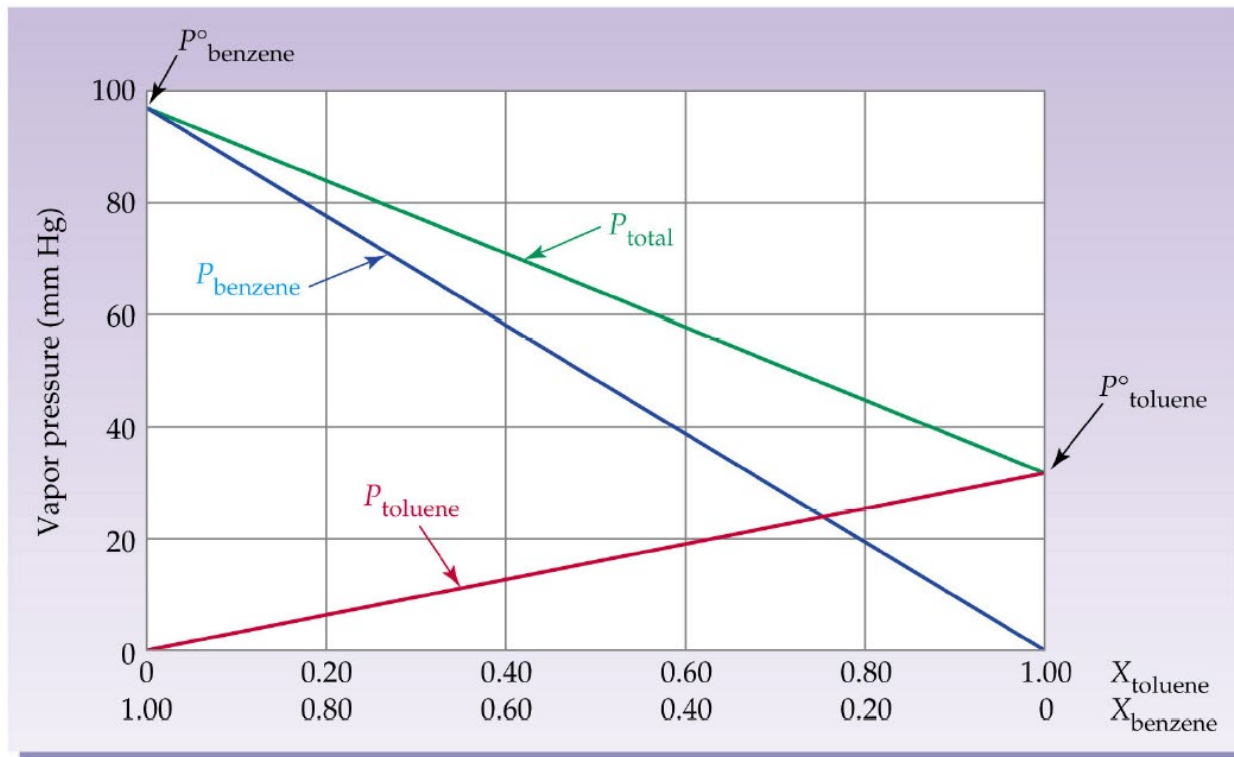
**benzene-toluene, quite ideal (similar to Fig 9.2 E&R) !!**

## Raoult's Law of Ideal Solutions

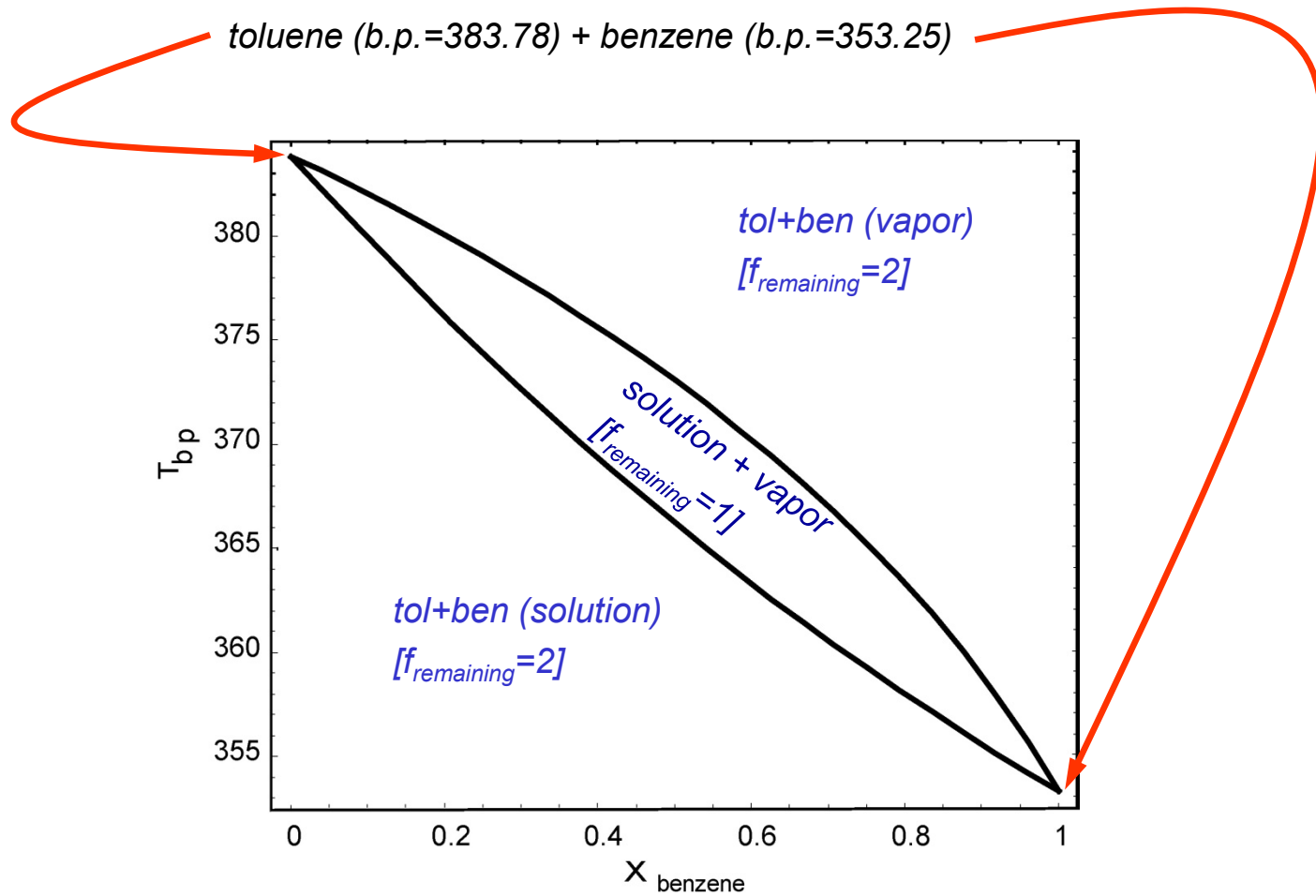
$$P_A = X_A^{(\ell)} P_A^\bullet \quad P_B = X_B^{(\ell)} P_B^\bullet$$

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

## 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

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

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

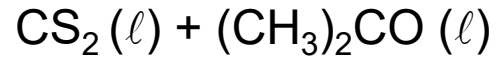
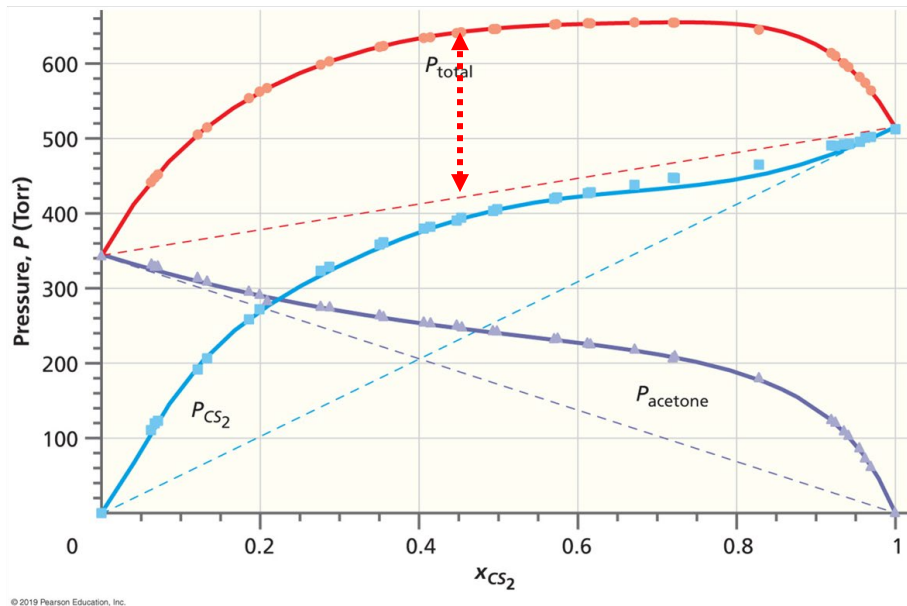
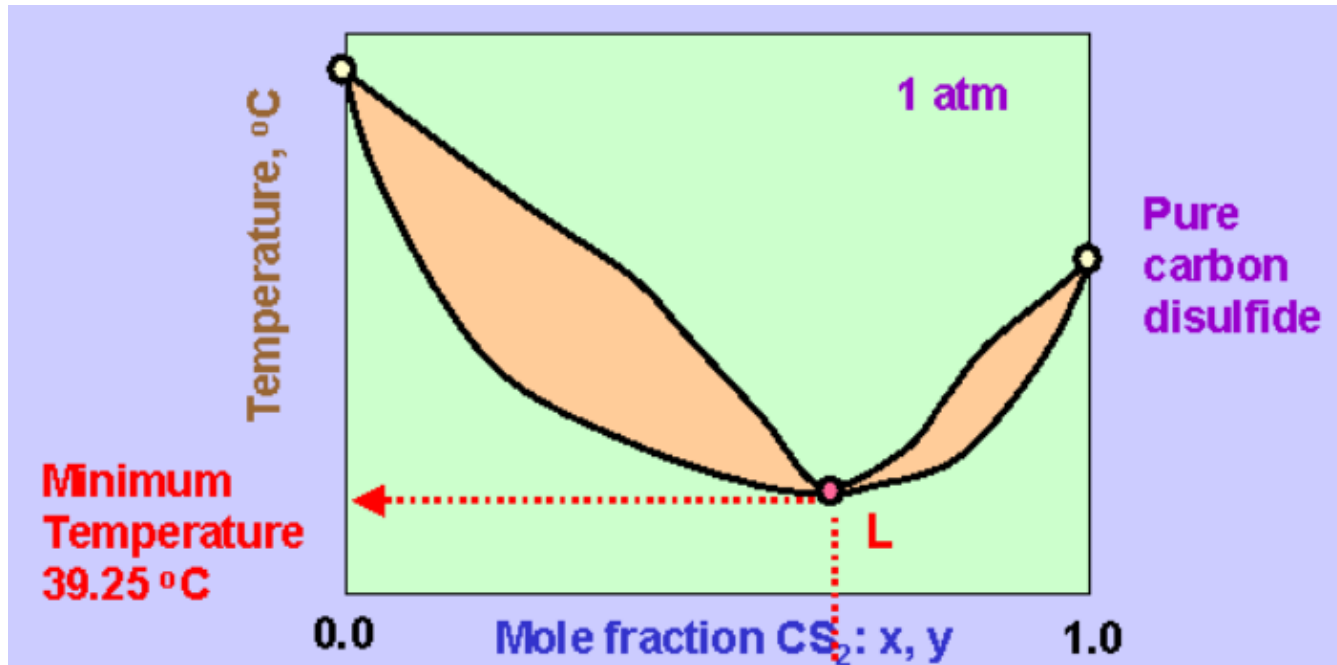


Figure 9-13 Deviations from Raoult's law. The data in Table 9-3 are plotted versus  $x_{\text{CS}_2}$ . Dashed lines show the expected behavior if Raoult's law were obeyed



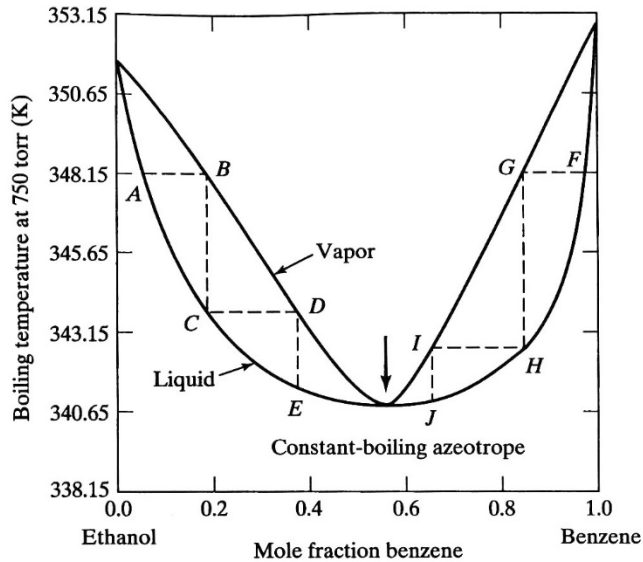
- **positive deviations** from Raoult's Law: **smaller forces between components than 'within' components**
- **total pressure greater than ideal solution**

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

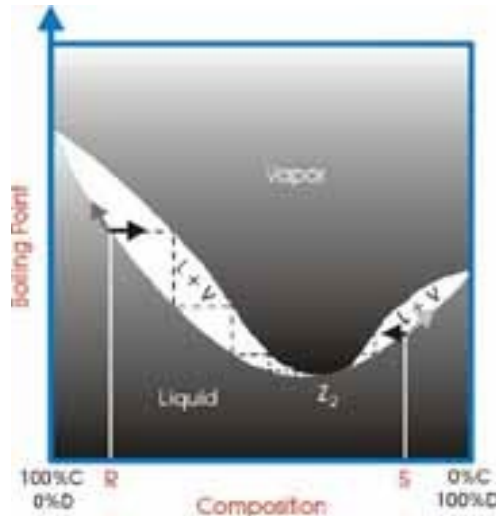


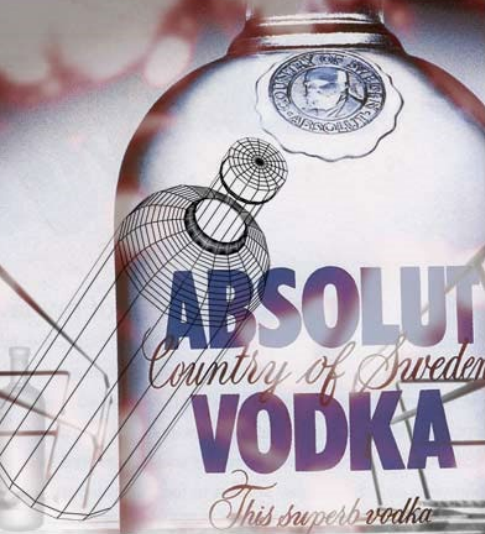
<http://www.separationprocesses.com/Distillation/Fig011b.htm>

# low boiling azeotrope

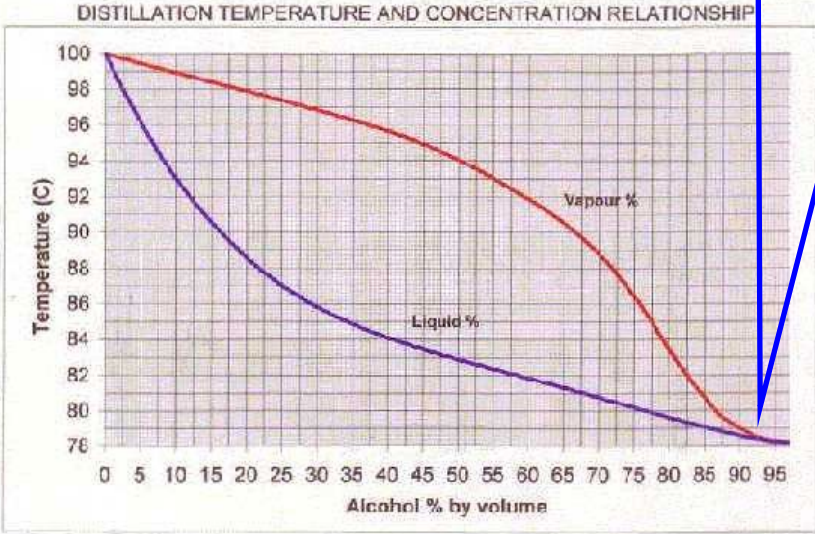
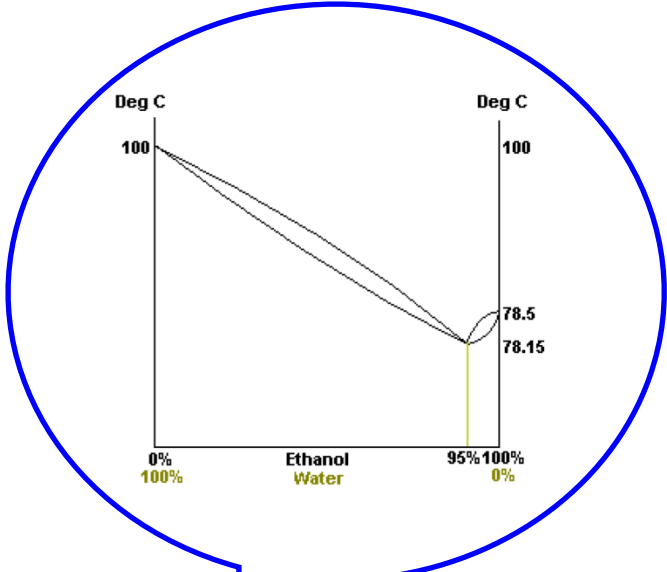


- weaker between component forces ( $A \leftrightarrow B$ ) (than  $A \leftrightarrow A$ ,  $B \leftrightarrow B$ )
- fractional distillation leads to constant boiling azeotrope in vapor
- and (in *pot* after azeotrope boils off)
  - $(X_A)_{\text{initial}} > (X_A)_{\text{azeotrope}}$  pure A
  - $(X_A)_{\text{initial}}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



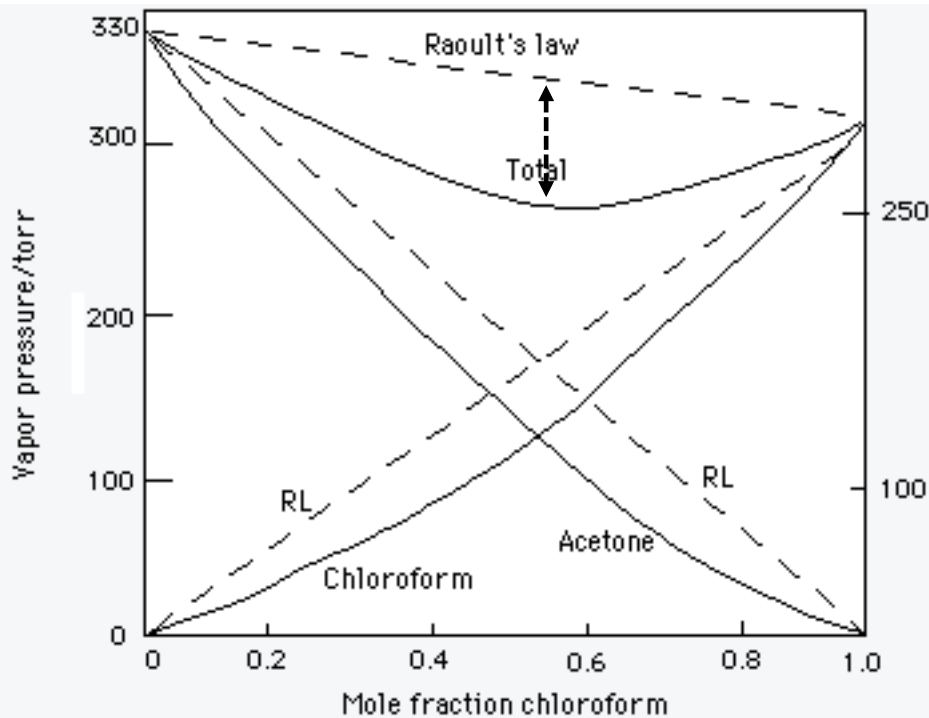
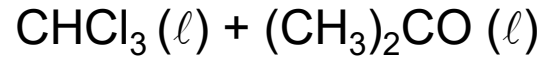


# Water-Ethanol Mixture



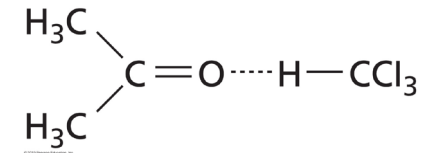
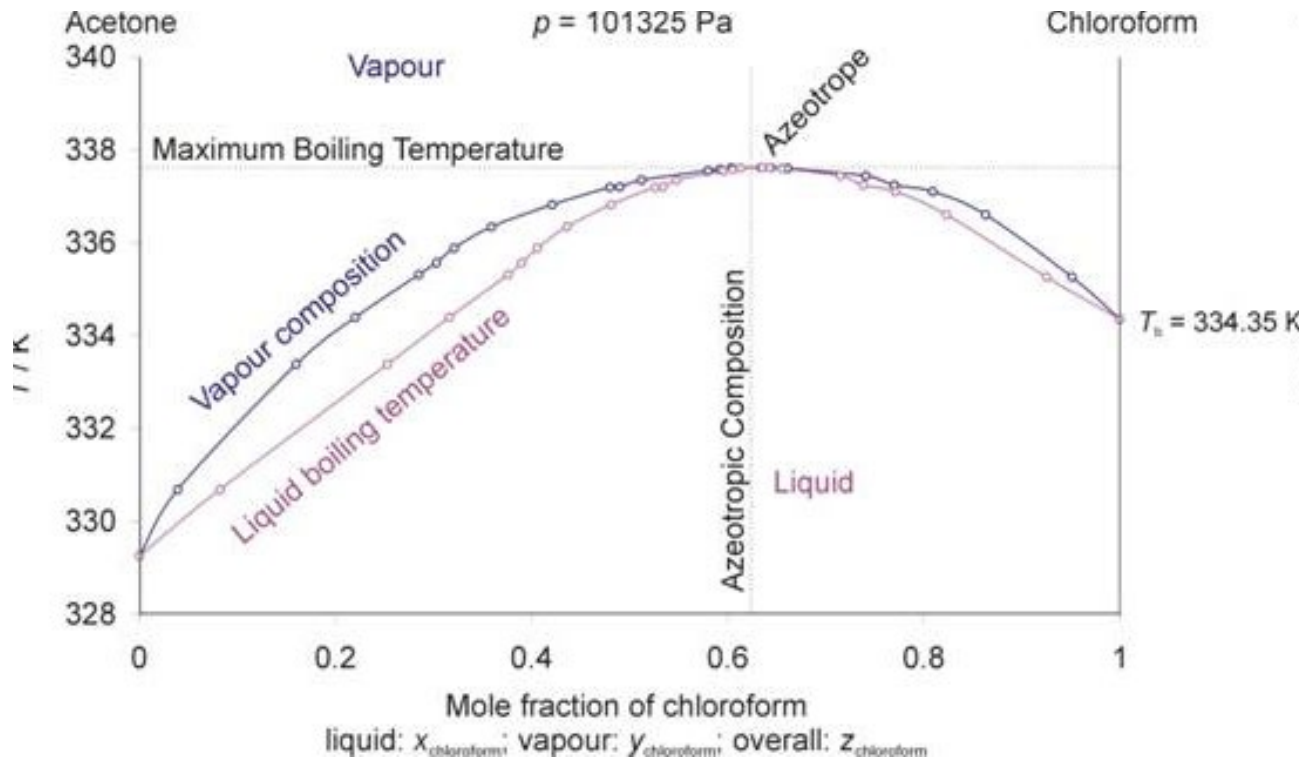
For the water-ethanol mixture, the azeotrope concentration corresponds to ~95% of ethanol in the mixture. This is the limit that can be reached by distillation of a less-alcohol-rich mixture.

# non-ideal solutions : negative deviations from ideal solution



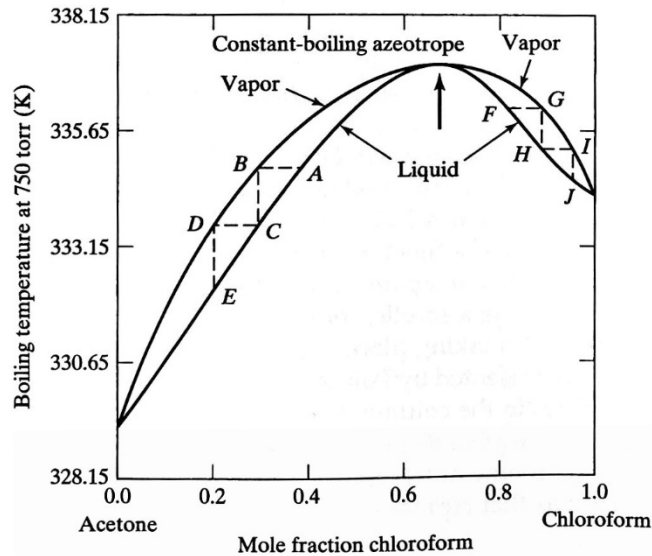
- negative deviations from Raoult's Law: greater forces between components than 'within' components
- total pressure lower than ideal solution

**acetone-chloroform: negative deviation  $\Rightarrow$  high boiling azeotrope**



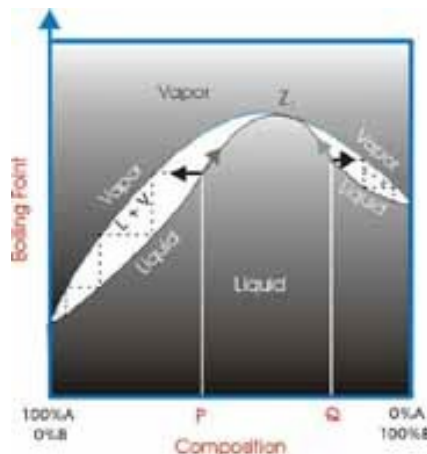
*Figure 9-8 Hydrogen bond formation between acetone and chloroform. The relatively strong bonding between species leads to the formation of a maximum boiling azeotrope*

# 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

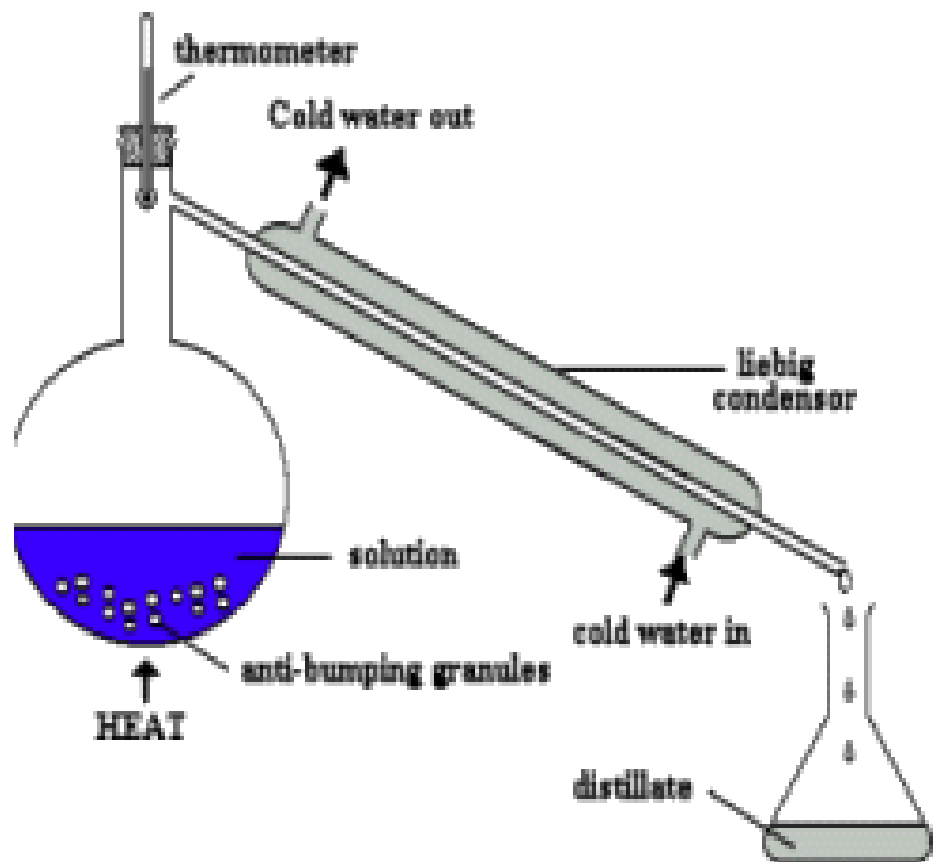
- $(X_A)_{\text{initial}} > (X_A)_{\text{azeotrope}}$  pure A
- $(X_A)_{\text{initial}} < (X_A)_{\text{azeotrope}}$  pure B



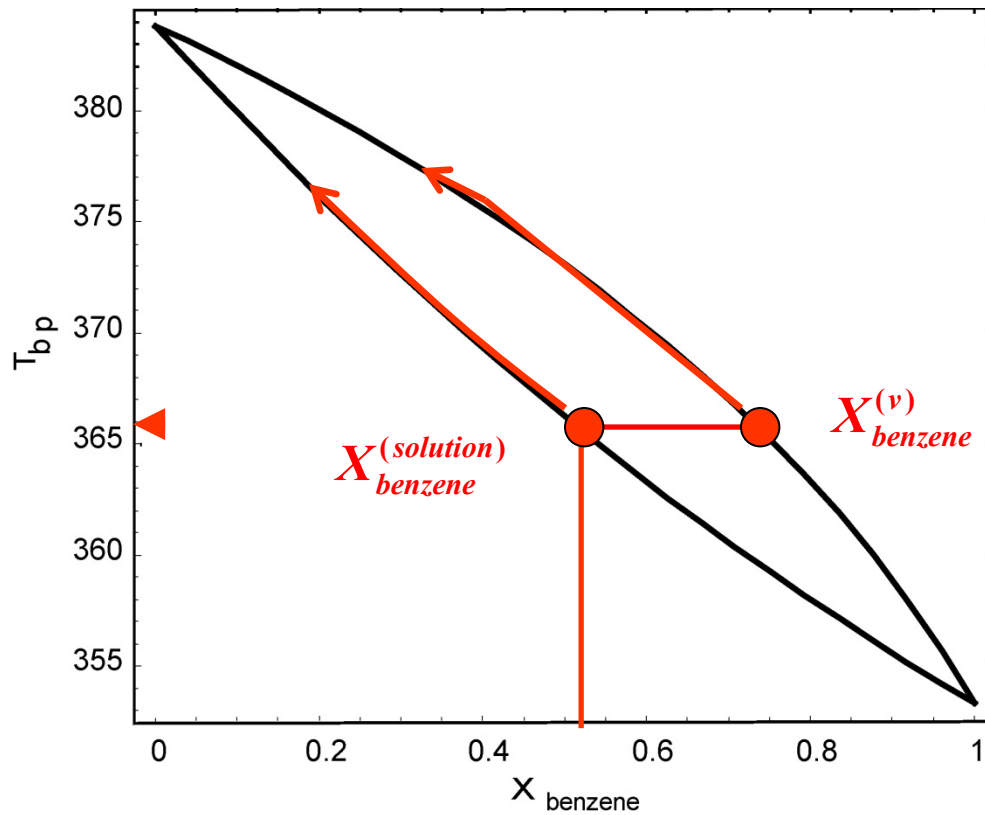


## *simple distillation*

---



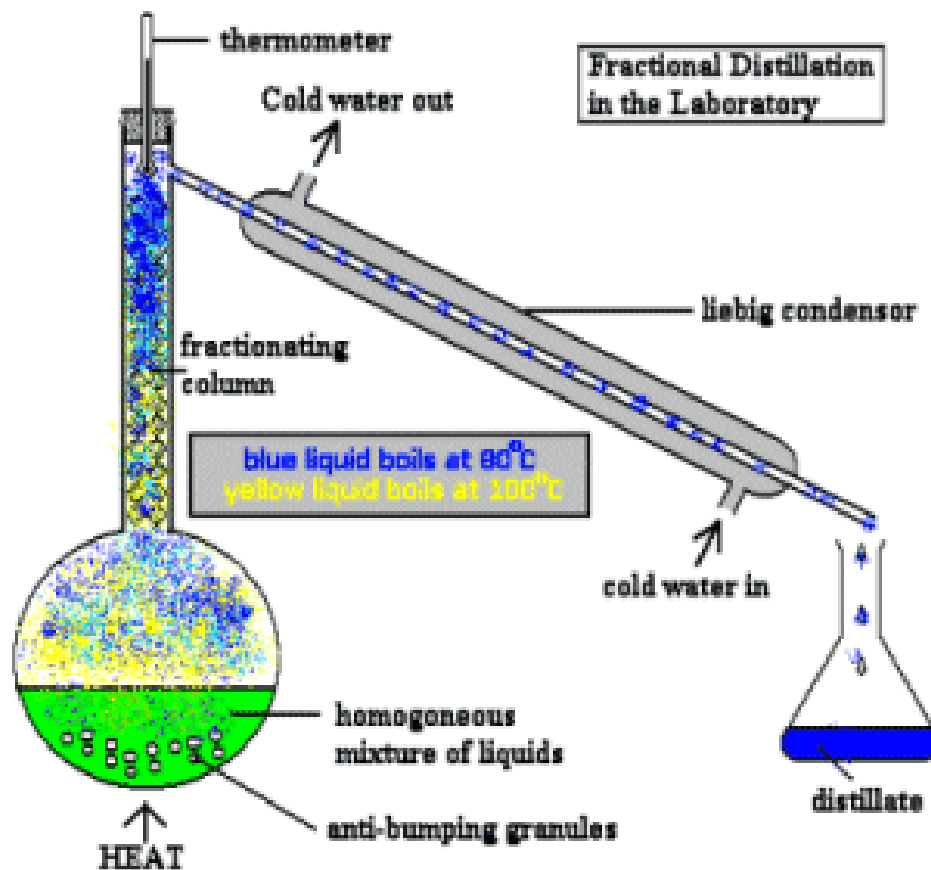
*simple distillation (one evaporation;  $T_{bp}$  varies as  $X$  changes)*



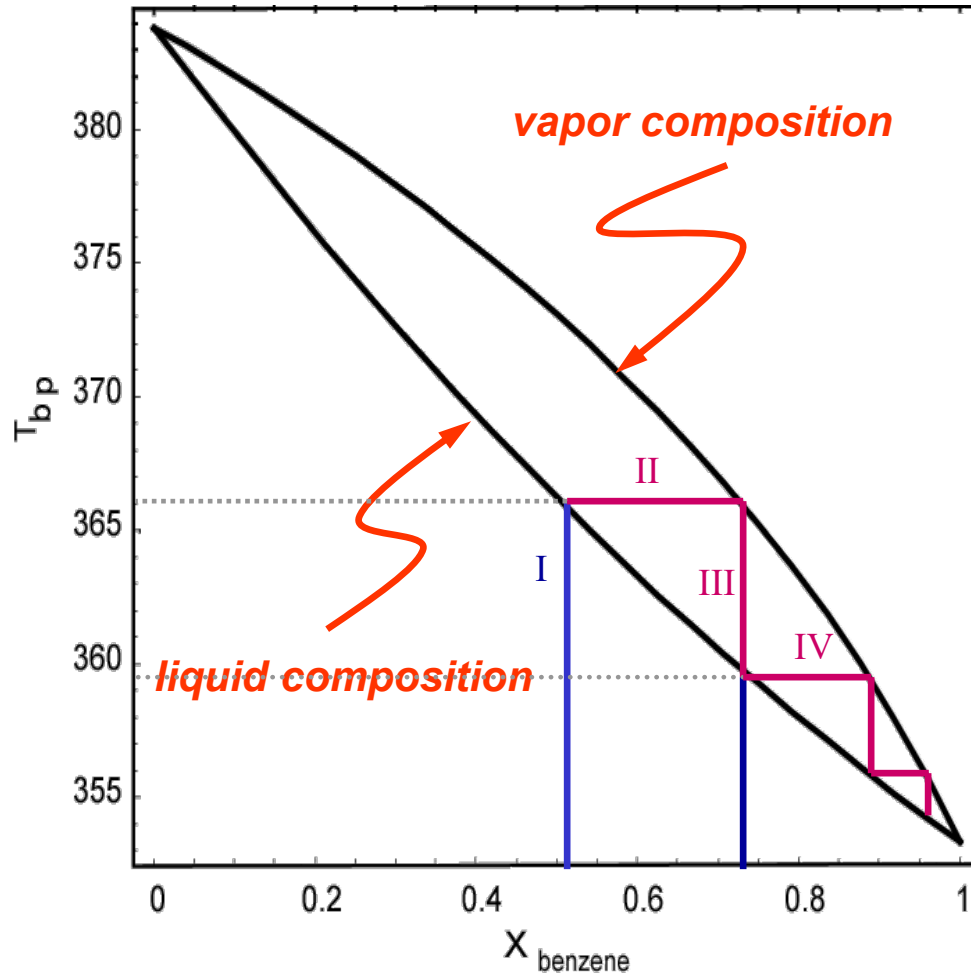
*add heat*  
 $X_{benzene}^{(solution)}$  *decreases*  
 $T_{bp}$  *increases gradually*

$X_{benzene}$

# *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  $X_{benzene}^v \approx .88$

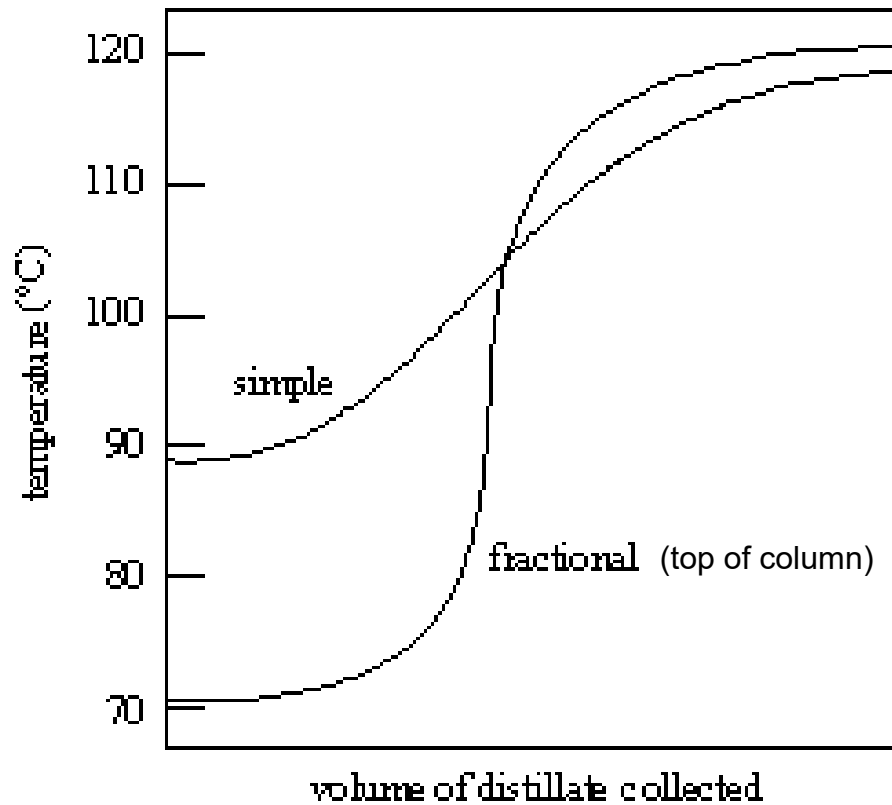
V. etc, ...

VI. approaches

$X_{benzene} = 1$       20

## *T vs progress for a distillation*

---

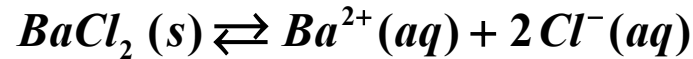


<http://www.uwlax.edu/faculty/koster/Image119.gif>

# **Electrolytes and Debye-Huckel Theory**

## activity coefficients for ions (HW8 #58)

---



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

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

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

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

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

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

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

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

# Debye-Hückel Theory

---

- 'a priori' calculation of activity coefficients,  $\gamma_{\pm}$ , for ions
- expect  $\gamma_{\pm} < 1$  since ions not independent [effective concentration reduced;  $a_{\pm} < c_{\pm}$ ]
- $\mu$  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  $\Omega$  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<sub>4th</sub>: Eqn 10.32 with  $\kappa$  from Eqn. 10.29]



# 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  $\kappa$  from Eqn. 10.29]

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

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

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

## from cumulative review

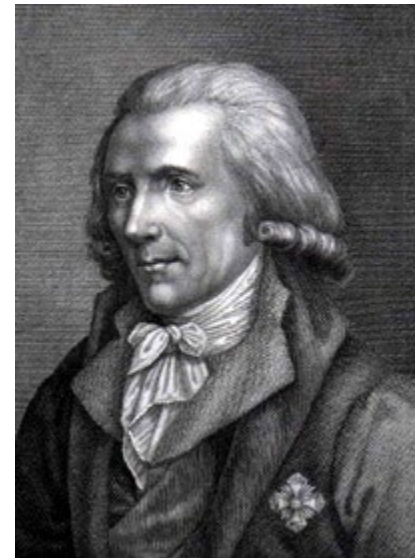
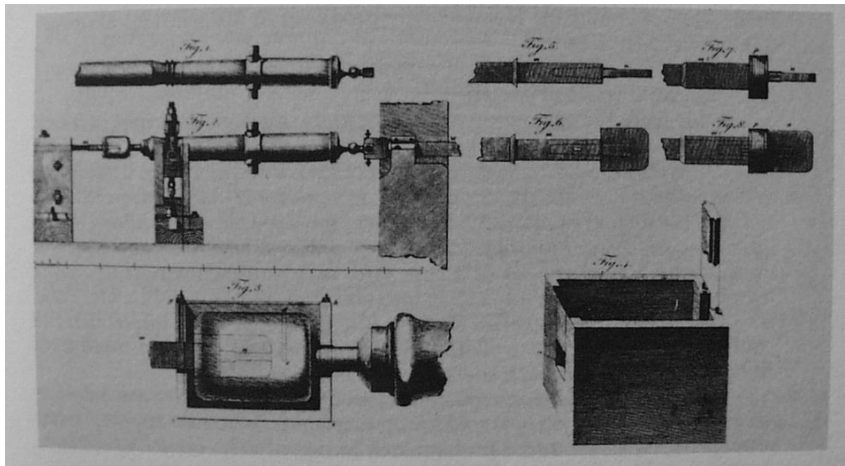
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- Concluding factoids
  - Thermodynamics is useful *whole quarter !!*
  - Electrical potential across membranes (e.g. neurons) can be calculated using Nernst equation *slides 2-3*
  - Non-idealities in solutions
  - Azeotropes and eutectics: constant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

## 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.)



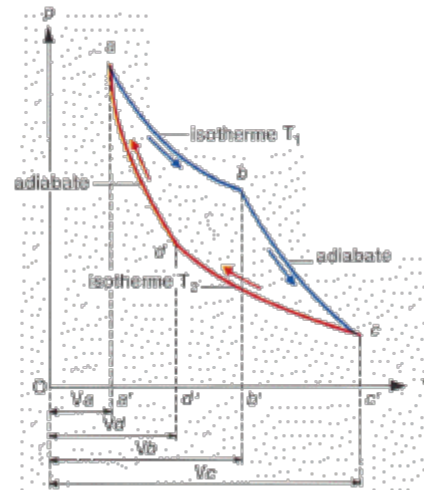
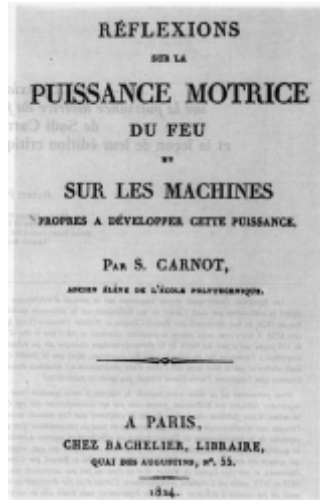
$$dU = \vec{d}q - PdV + dw_{other}$$

$$\oint dU = 0$$

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

# observations: mechanical efficiency of steam engine

- Sadi Carnot, 1824
- efficiency of engines



### microstates and disorder



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

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

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

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

$$\oint dS = 0$$

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

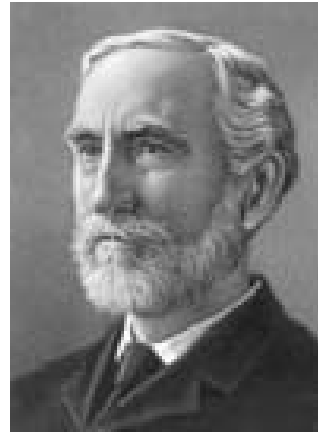
$$dH = TdS + VdP + dw_{\text{other}}$$

## *“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

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

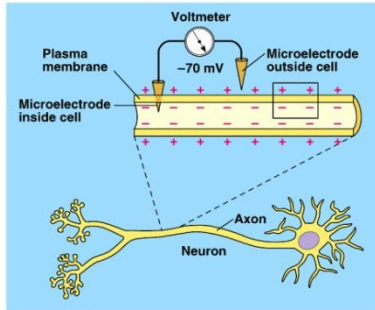
$$\frac{\Delta G_{T,P}}{T} = \underbrace{\frac{\Delta H_{T,P}}{T}}_{-\Delta S_{surroundings}} \underbrace{-\Delta S_{T,P}}_{-\Delta S_{system}}$$

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

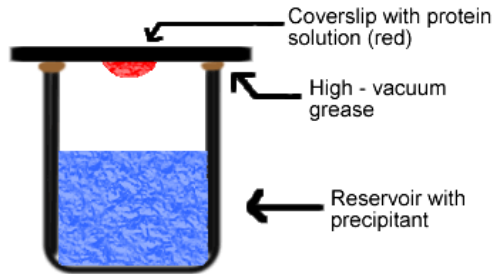
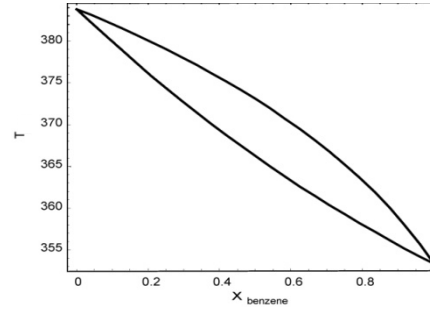
$$dA = -SdT - PdV + dw_{other}$$



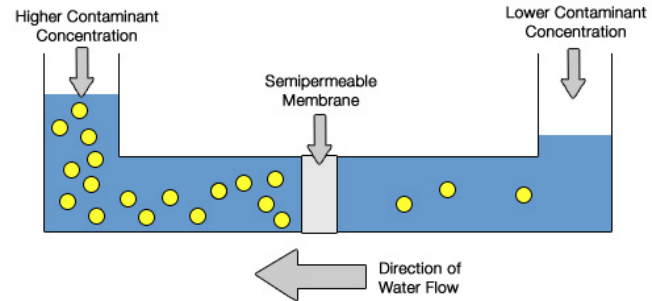
# Applications



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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

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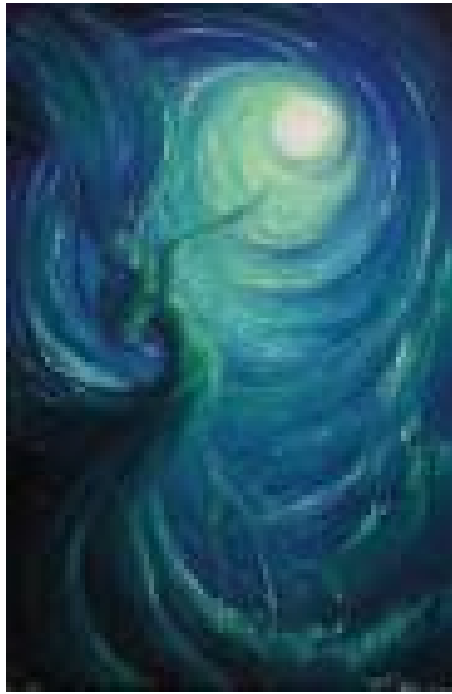
- Conceptual and 'analytical math' from throughout term
- Problems concentrate on material since last exam
  - Partial molar quantities,  $\Delta\mu$  for variable composition
  - Ideal Solutions and corrections for non-ideality
  - Phase equilibria and phase diagrams
    - one-component, relationship of T and P for one component equilibrium
    - two-component (solid  $\rightleftharpoons$  solution and solution  $\rightleftharpoons$  vapor )
  - Colligative properties (**HW8**)
  - Electrochemistry (**HW8**)
    - $\Phi$  and  $\Delta G$ ,  $\Delta\mu$
    - 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"> <li>• Sample Final on eCommons</li> <li>• HW#9 Solutions on eCommons</li> <li>• Review Weeks 8-10 on WWW</li> </ul>		
Sunday, 16 March	<ul style="list-style-type: none"> <li>• Sample Final Key on eCommons</li> </ul>		
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 <b>Thimann 1</b> Review Session <i>Switkes</i>		
Tuesday, 18 March	4:00-5:00 PM	145 PSB	<b>Last Chance</b> Review Office Hours <i>Liu</i>
Wednesday, 19 March	10:00-12:00 AM	341 PSB	<b>Last Chance</b> Review Office Hours <i>Mednick</i>
<b>Thursday, 20 March</b>	<b>FINAL EXAM</b> <b>12:00-3:00 PM</b> <b>Classroom 1</b>		

Chemistry 163B  
Winter 2020  
help sessions  
Finals Prep



**FINIS**

(except)

**MUCH  
Thanks To  
two GREAT TAs**

**Evan**

and

**Plam**



## Some Important Points for Chemistry 163B On-Line Final

Get Ready for 19<sup>th</sup> 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, 16<sup>th</sup> March, 9AM-9PM I will make CANVAS Trial test#2 available for you. Here I have taken a couple of questions from the "Sample Final Exam" (old fashion pdf on CANVAS, available now, KEY on 15<sup>th</sup> March) and converted them to how our on-line final will look. Please SUBMIT your responses so Evan, Pam, Jerah, and I can shake out our 'hand grading' protocols. **YOU 'SCORE' ON THIS TRIAL EXAM IS NOT A PART OF YOUR CLASS GRADE.**

FOR THE EXAM 19<sup>th</sup> 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 materials on the WWW
- Points for problems indicating "marked by hand" will 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