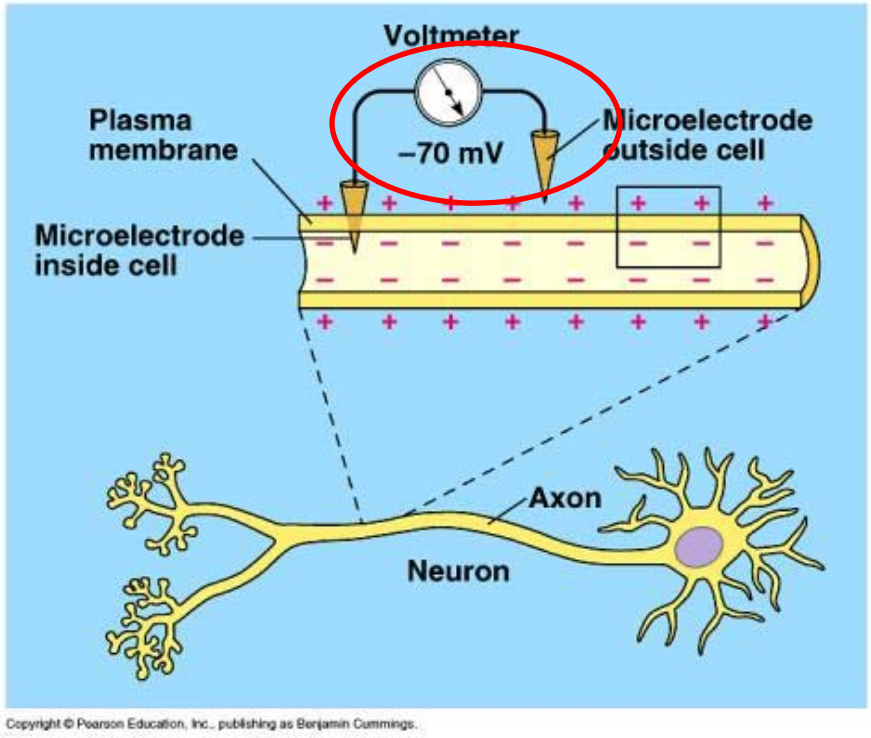
Chemistry 163B

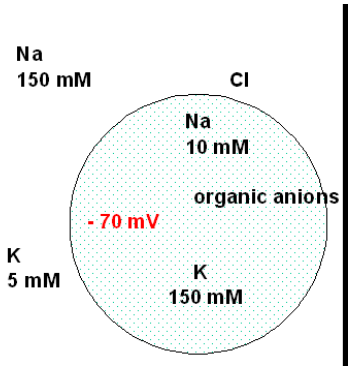
Concluding Factoids

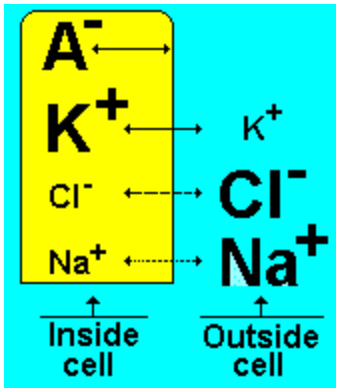
and

Comments

neuron, resting potential





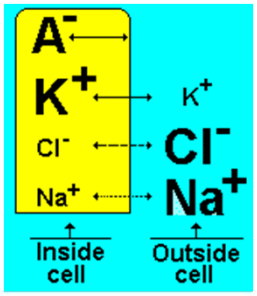


http://projects.gw.utwente.nl/pi/sim/Bovt/concep4.gif

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

resting potential and Nernst Equaiton

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



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 μM	2 mM

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

$$\Phi^\circ = 0$$

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

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

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

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

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

http://www.cellbio.wustl.edu/faculty/huettner/models.htm

Gibbs-Duhem

the partial molar quantities do not vary independently

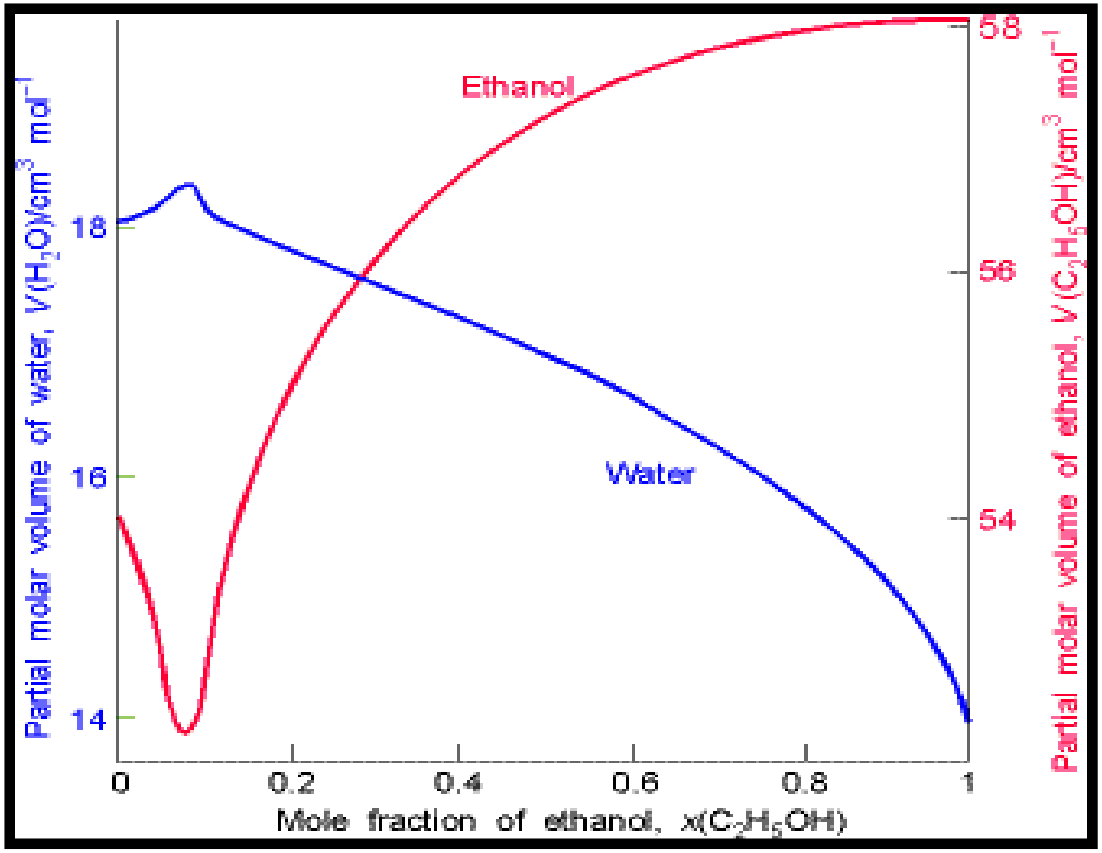
Gibbs-Duhem

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

what are

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

when a and b form an ideal solution ?



do ideal solutions obey the Gibbs-Duhem relation?

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

non-ideal solutions

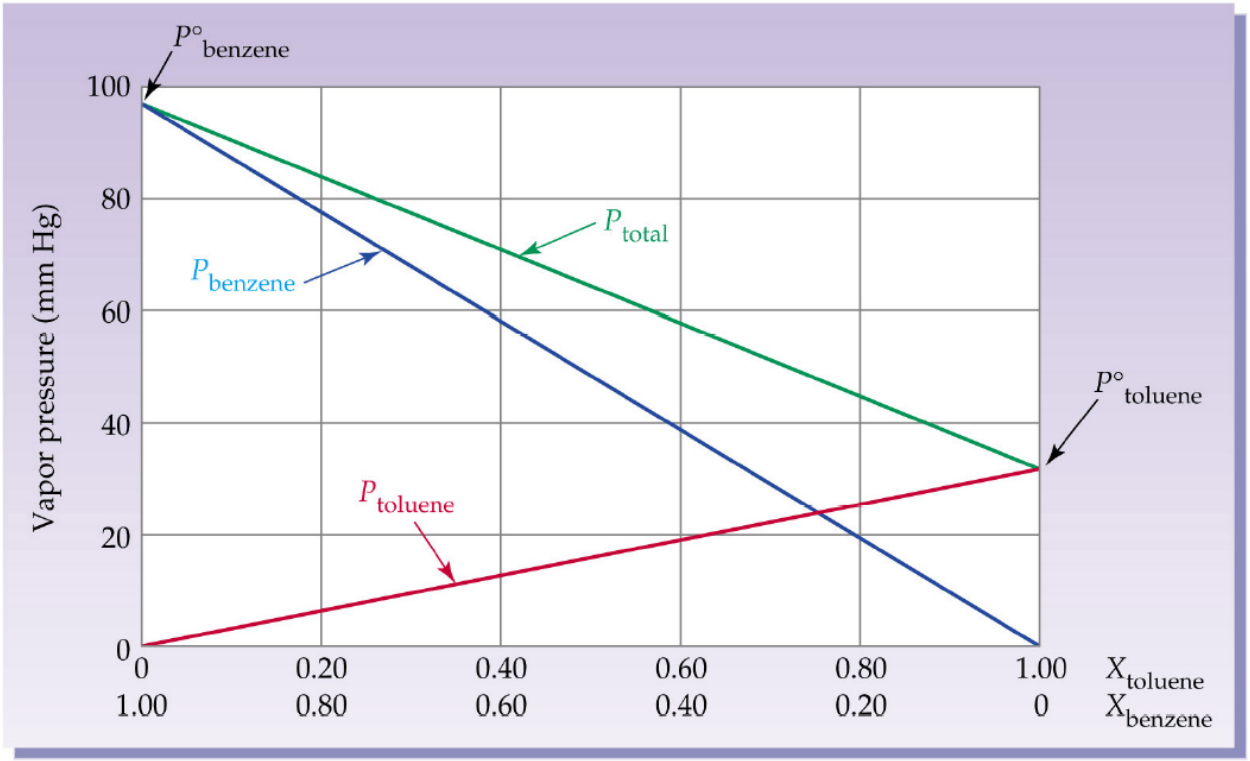
benzene-toluene, quite ideal (similar to Fig 9.2 E&R) !!

Raoult's Law of Ideal Solutions

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

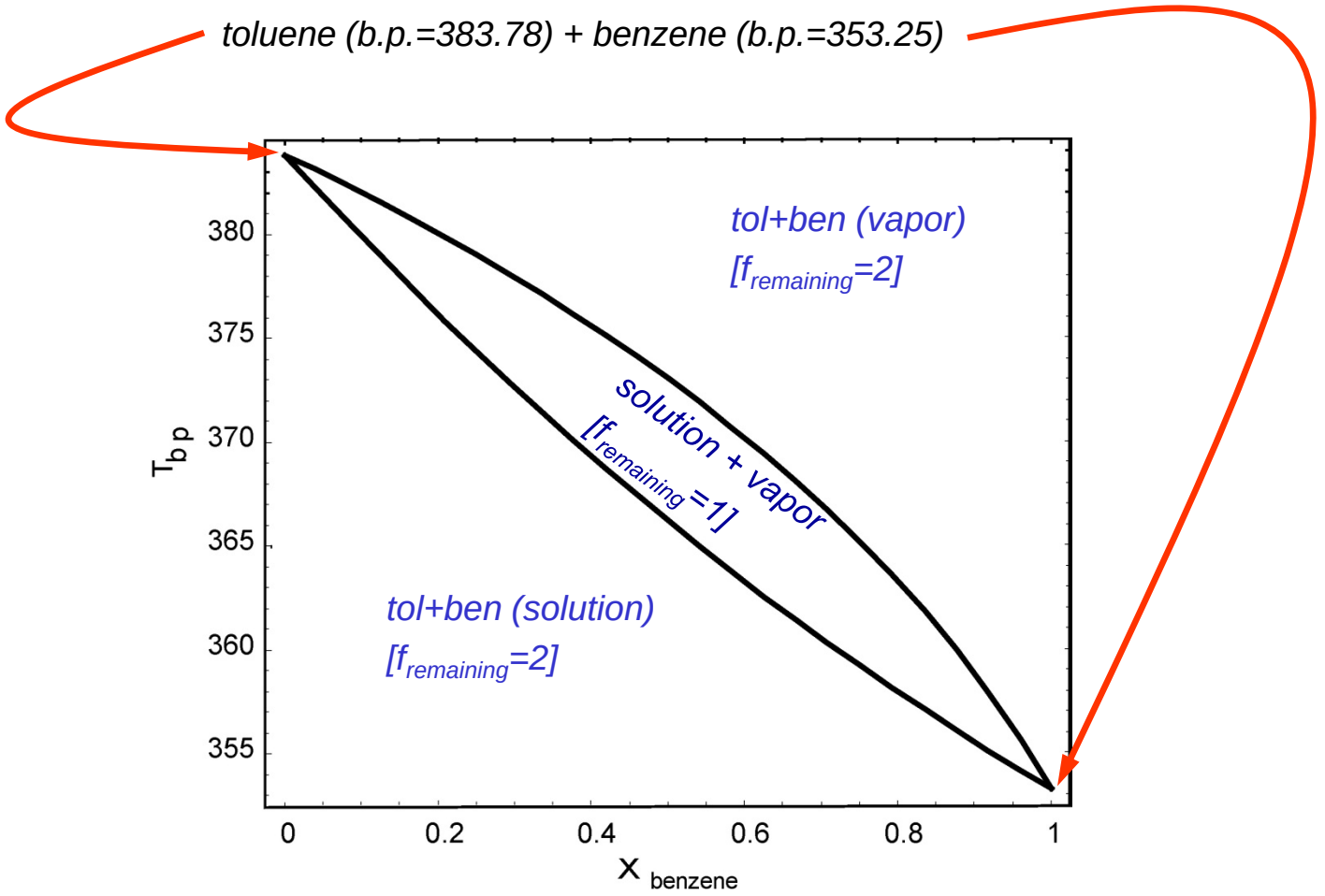
$$P_{total} = X_A^{(\ell)} \left(P_A^{\bullet} - P_B^{\bullet} \right) + P_B^{\bullet}$$

Benzene and Toluene



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

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



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

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

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

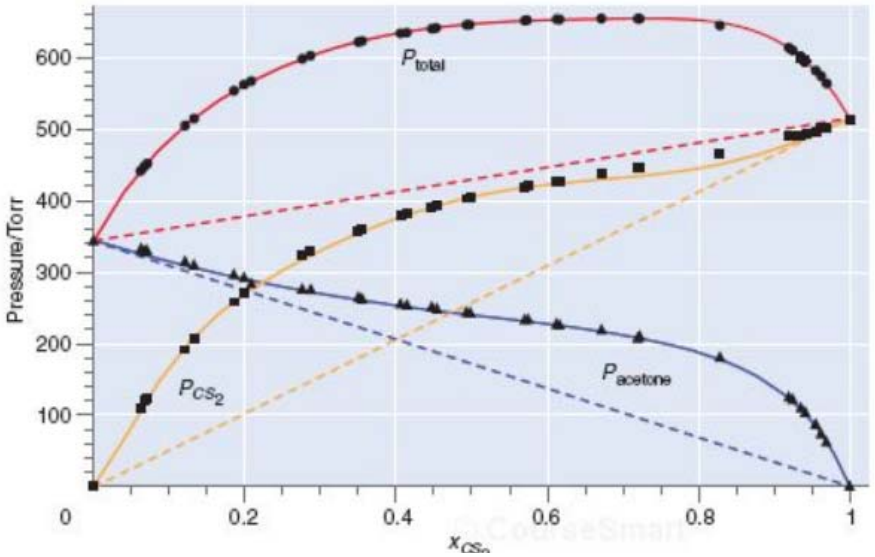
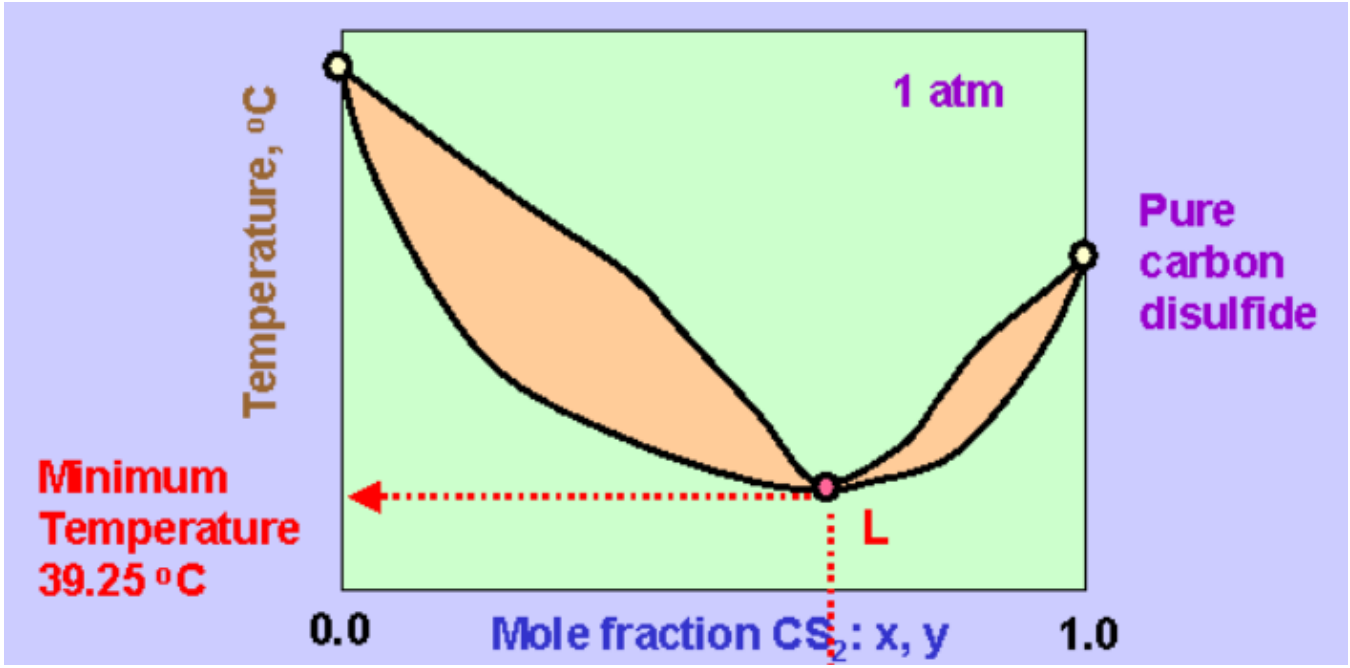


FIGURE 9.13

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.

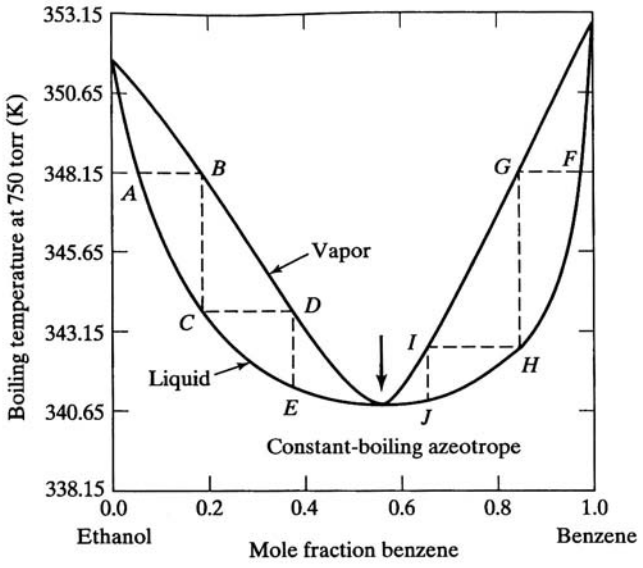
- positive deviations from Raoult's Law: smaller forces between components than 'within' components
- total pressure greater than ideal solution

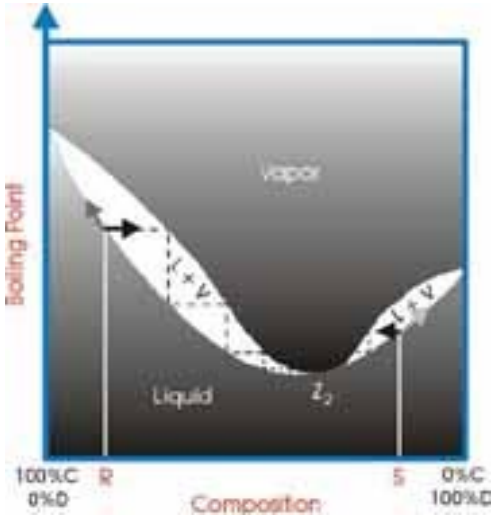
acetone-carbon disulfide: positive deviation ⇨ low boiling azeotrope



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

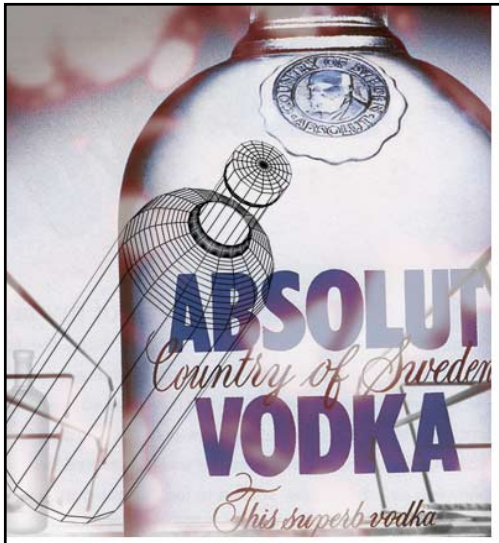
low boiling azeotrope



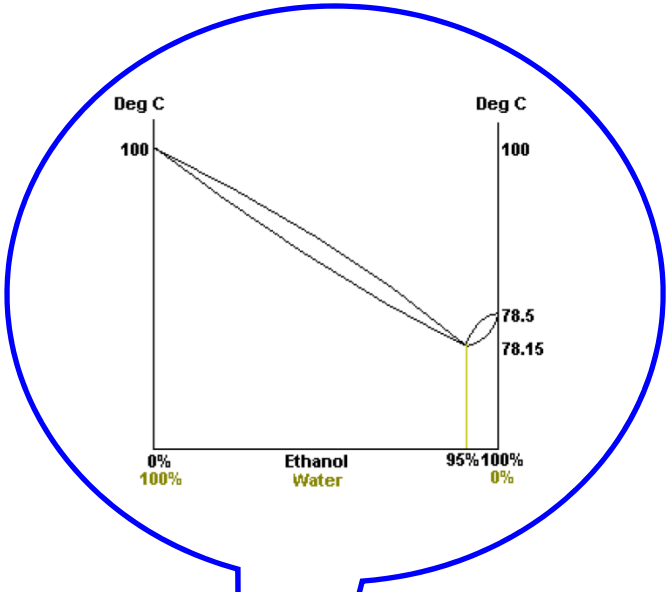


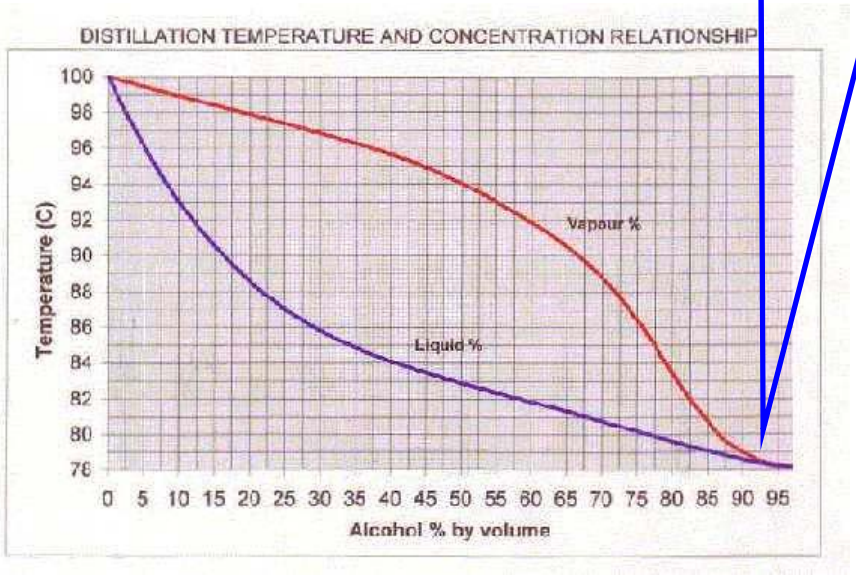
- weaker between component forces (A↔B) (than A ↔A, B ↔B)
- fractional distillation leads to constant boiling azeotrope in vapor
- *and (in **pot** after azeotrope boils off)*
  - $(X_A)_{initial} > (X_A)_{azeotrope}$ pure A
  - $(X_A)_{initial} < (X_A)_{azeotrope}$ pure B

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



Water-Ethanol Mixture

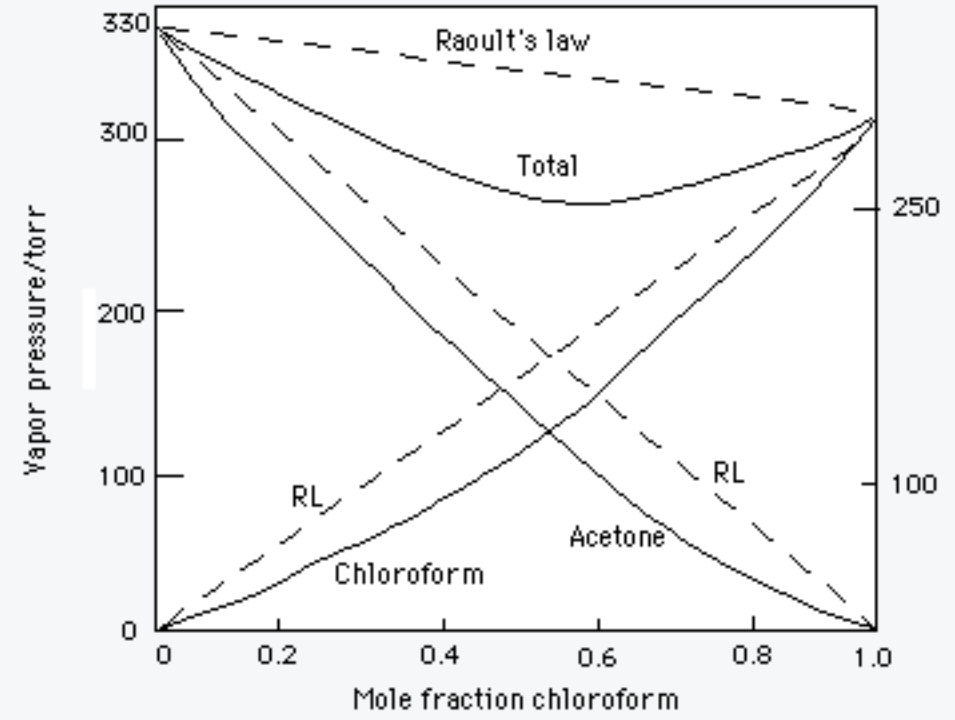




For the water-ethanol mixture, the azeotrope concentration corresponds to ~95% of ethanol in the mixture. This is the limit that can be reached by distillation of a less-alcohol-rich mixture.

non-ideal solutions : negative deviations from ideal solution

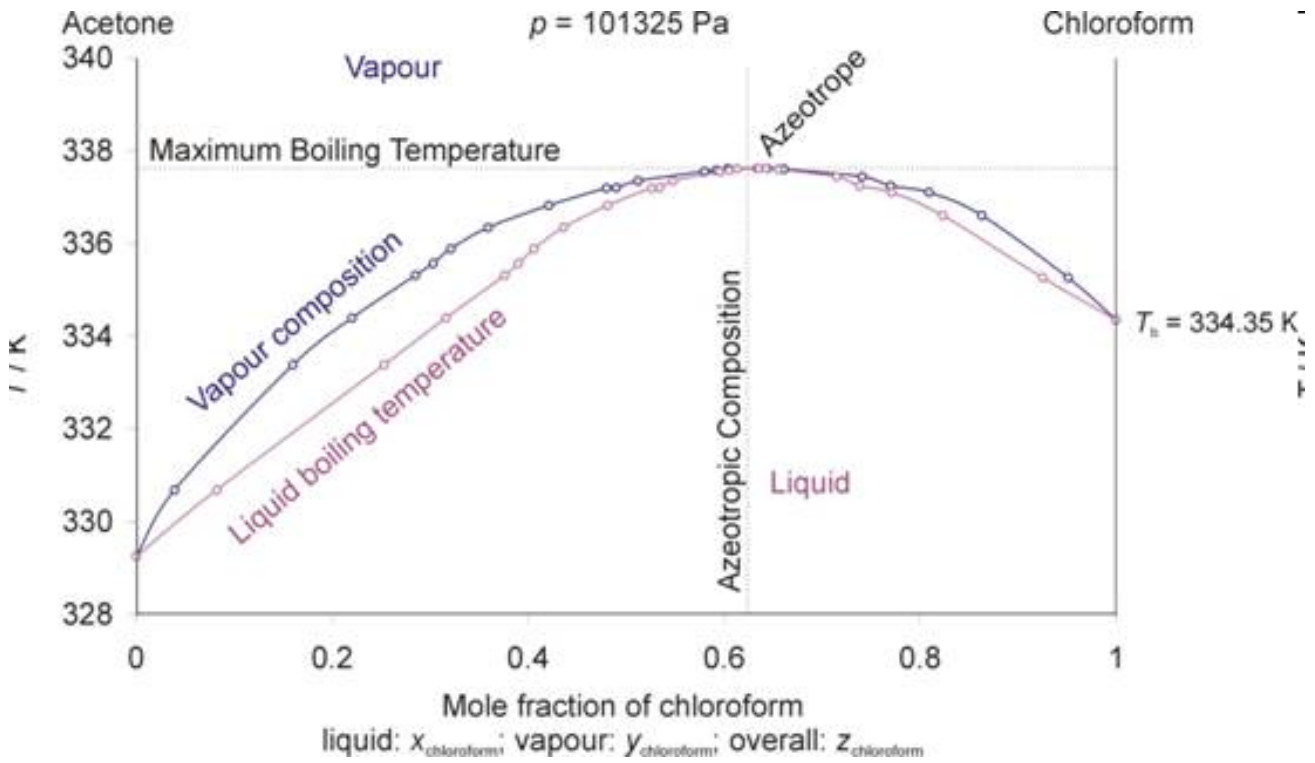
$CHCl_3\ (\ell) + (CH_3)_2CO\ (\ell)$



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

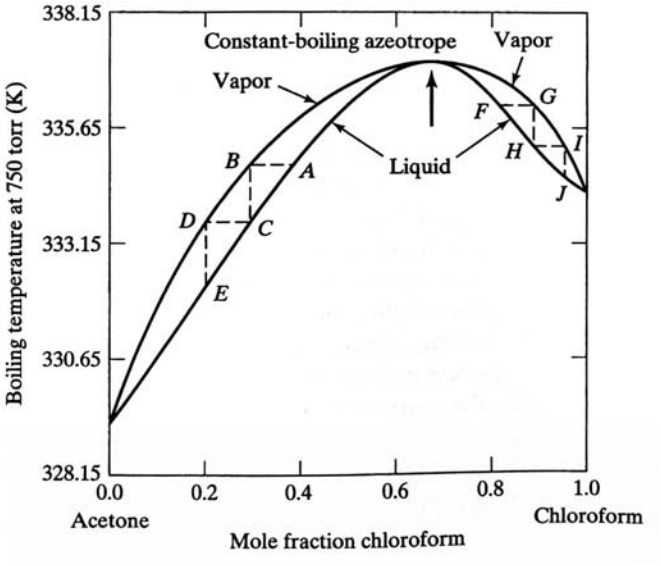
http://dwb4.unl.edu/Chem/CHEM869W/CHEM869WImages/raoult2.gif

acetone-chloroform: negative deviation ⇨ high boiling azeotrope



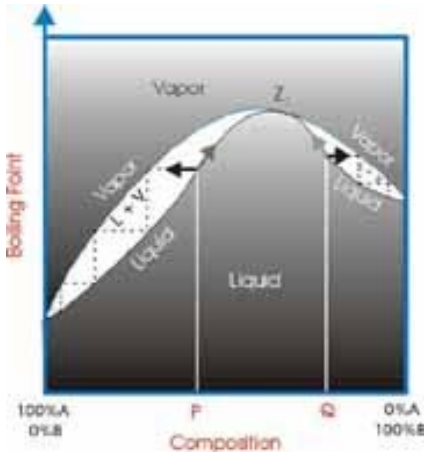
http://www.chm.bris.ac.uk/~chdms/Teaching/Chemical_Interactions/images/pic192.jpg

high boiling azeotrope



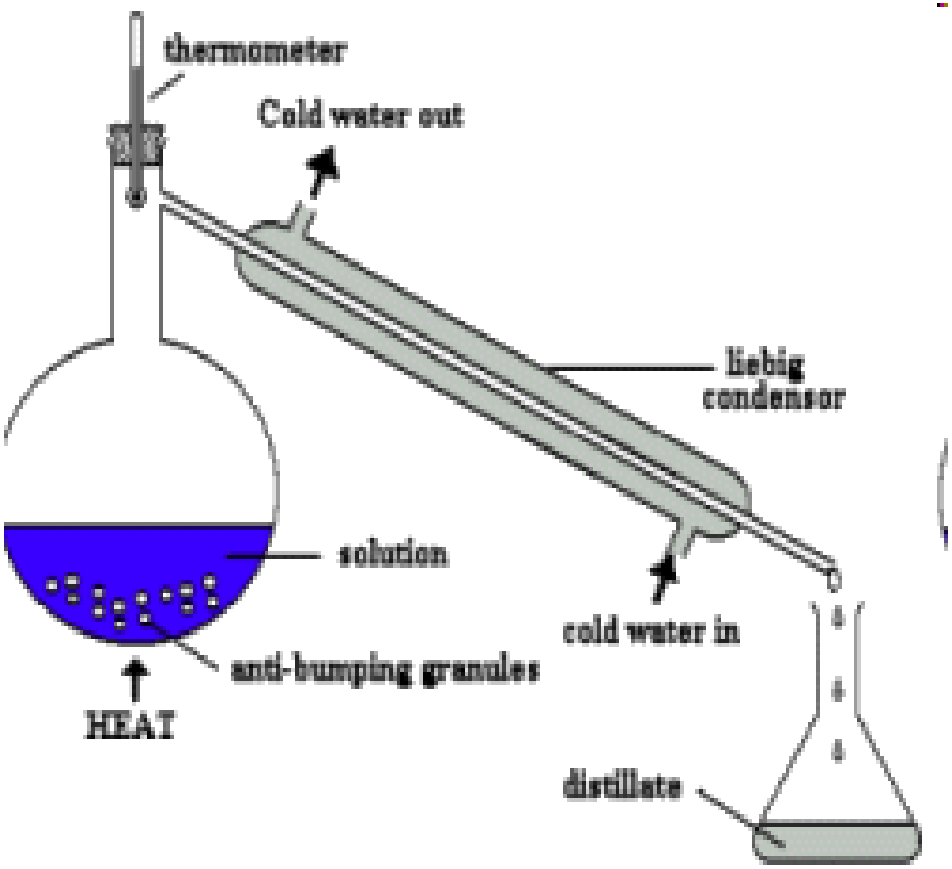
- stronger between component forces (A↔B) (than A ↔A, B ↔B)

- 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



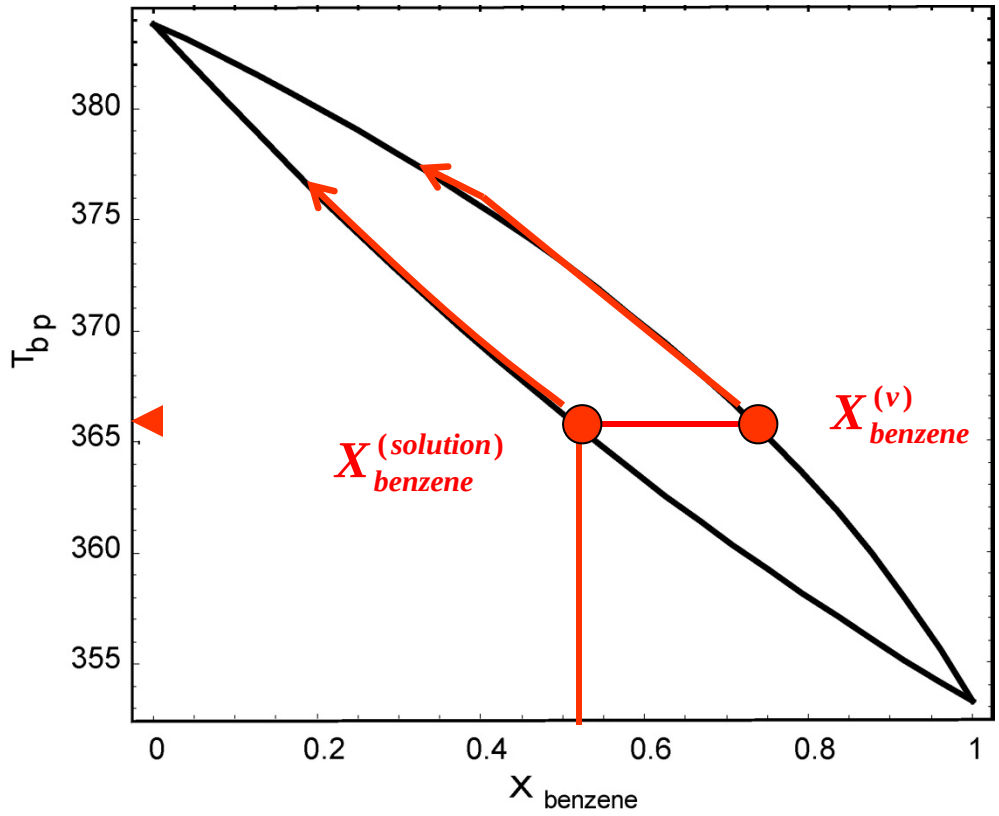
http://www.solvent--recycling.com/azeotrope_1.html

simple distillation



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

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



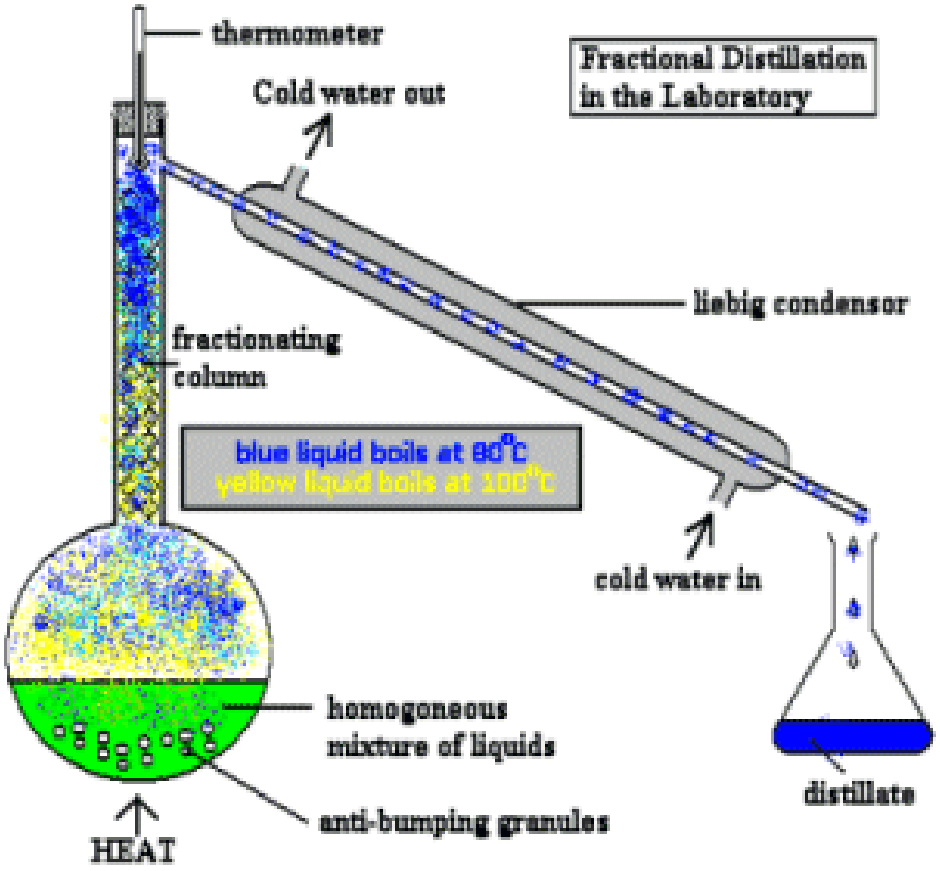
$X_{benzene}$

add heat

$X^{(solution)}_{benzene}$ ***decreases***

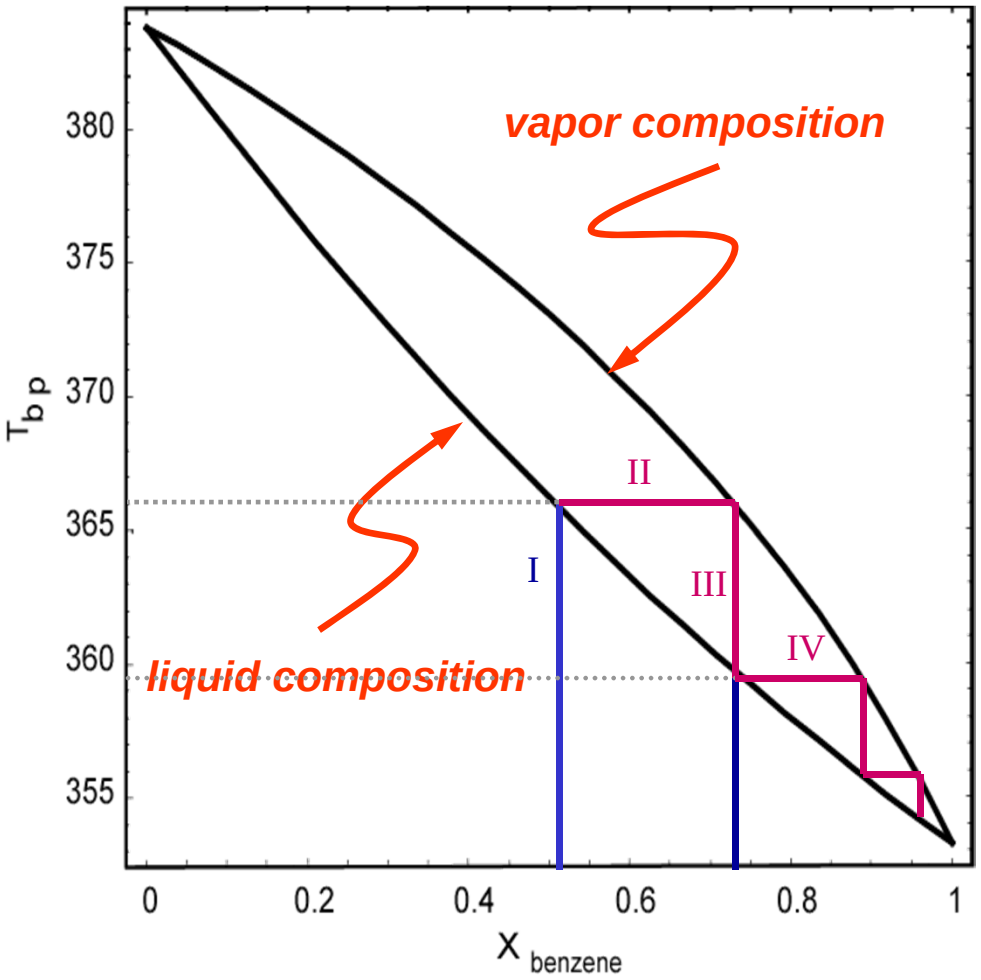
T_{bp} ***increases gradually***

fractional distillation



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

Fractional Distilation



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

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

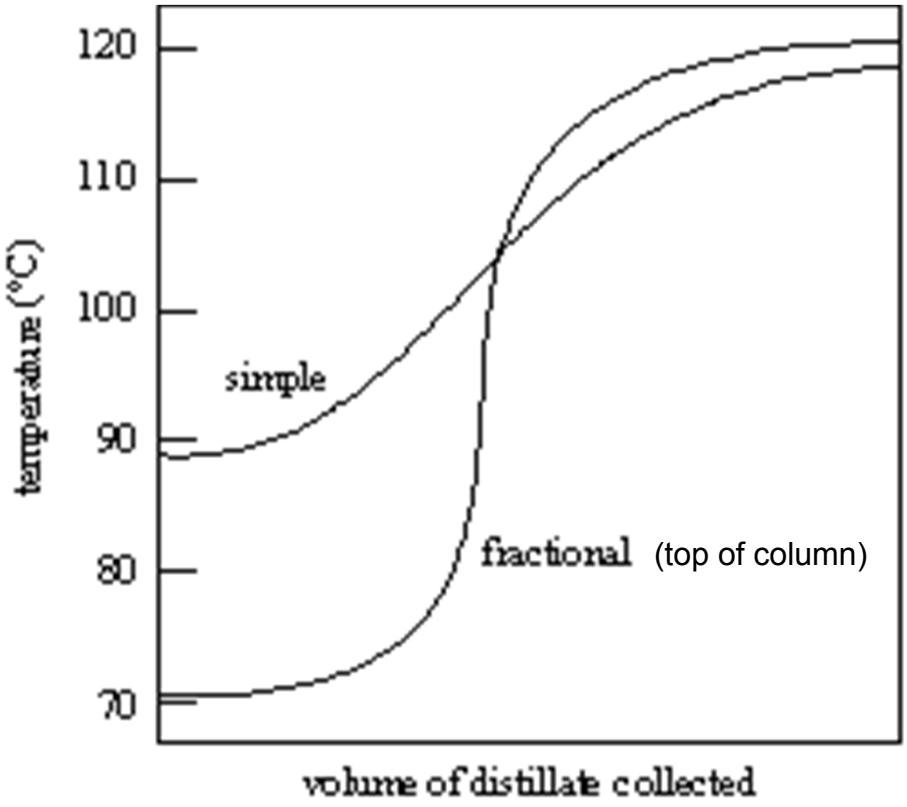
III. • condense $X^{\ell}_{benzene} \approx .72$
• $T_{bp} \approx 359.5$

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

V. etc, ...

VI. apporaches
$X_{benzene}=1$

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)

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

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

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

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

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

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

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

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

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

Debye-Hückel Theory

- 'a priori' calculation of activity coefficients, $\gamma_{\pm}$, for ions
- expect $\gamma_{\pm} < 1$ since ions not independent [effective concentration reduced; $a_{\pm} < c_{\pm}$]
- 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]

Debye-Hückel Theory

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

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

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

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

observations: thermo ≡ heat

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

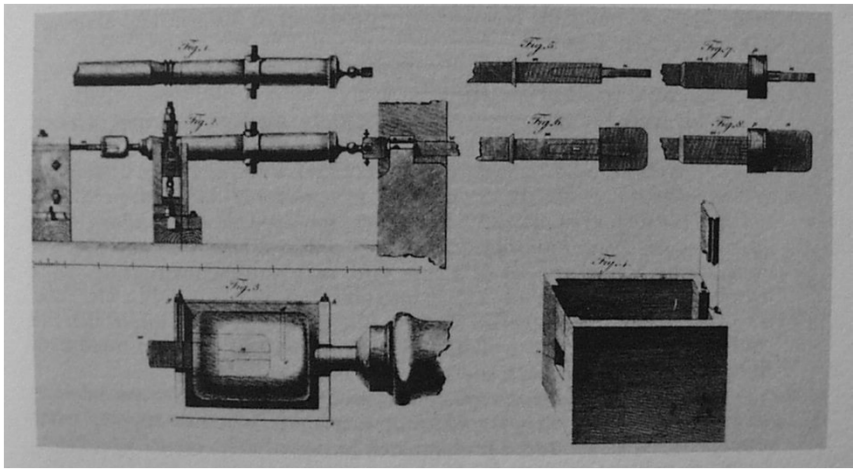


FIGURE 11. An illustration from Rumford's paper, "An Inquiry Concerning the Source of the Heat Which is Excited by Friction," showing the apparatus used by him in the cannon boring experiment. Figure 1, upper left, shows the cannon as received from the foundry, and Figure 2, below, shows it mounted in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

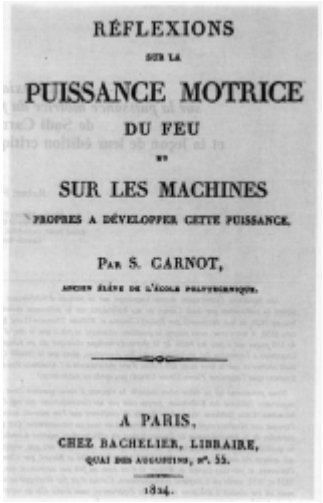
$$dU = đq - PdV + dw_{other}$$

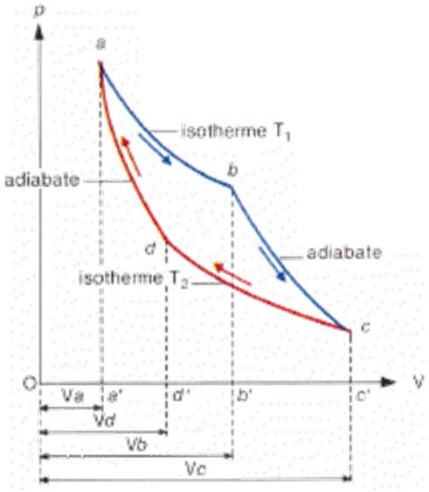
$$\oint dU = 0$$

$$dH = đq + VdP + dw_{other}$$

observations: mechanical efficiency of steam engine

- Sadi Carnot, 1824
- efficiency of engines


RÉFLEXIONS
SUR LA
PUISSANCE MOTRICE
DU FEU
ET
SUR LES MACHINES
PROPRES A DÉVELOPPER CETTE PUISSANCE.
PAR S. CARNOT,
A PARIS,
CHEZ BACHELIER, LIBRAIRE,
1824.



microstates and disorder

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

$$dS \geq \frac{\cancel{dq}}{T}$$

$$dS = \frac{\cancel{dq}_{rev}}{T}$$

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

$$\oint dS = 0$$

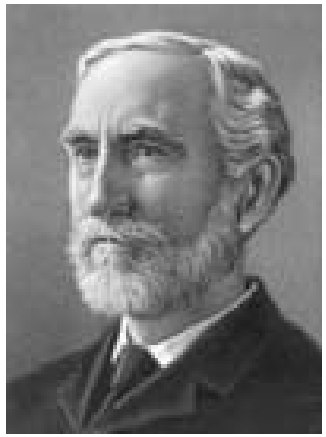
$$dU = TdS - PdV + dw_{other}$$

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

"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 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

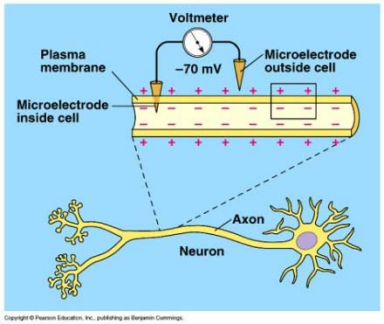
$$\Delta G_{T,P} = \Delta H_{T,P} - T\Delta S_{T,P}$$

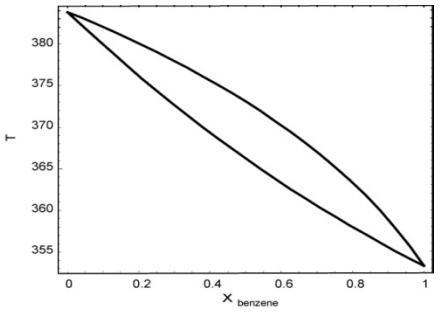
$$\frac{\Delta G_{T,P}}{T} = \underbrace{\frac{\Delta H_{T,P}}{T}}_{-\Delta S_{surroundings}} \quad \underbrace{-\Delta S_{T,P}}_{-\Delta S_{system}}$$

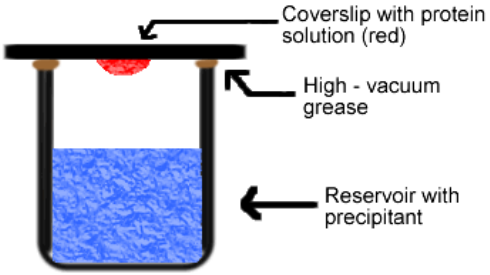
$$dG = -SdT + VdP + dw_{other}$$

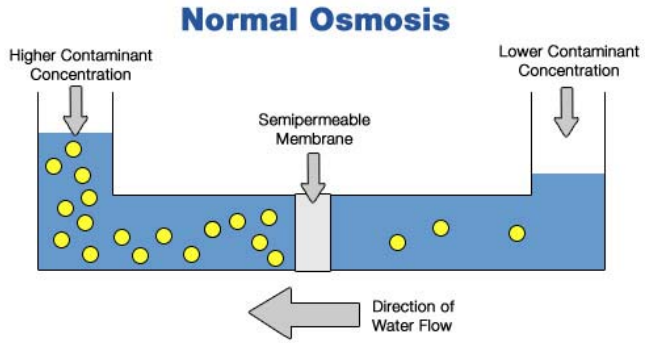
$$dA = -SdT - PdV + dw_{other}$$

Applications









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

Maxwell-Euler

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

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

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

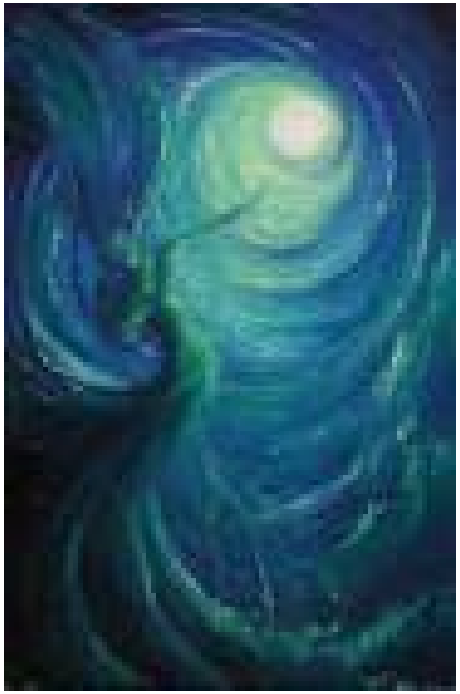
$$\left(\frac{\partial \ln K_{eq}}{\partial T} \right)_P = \frac{\Delta H^o_{reac}}{RT^2}$$

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 (**HW8**)
    - • Electrochemistry (**HW8**)
        - • Φ and ΔG, $\Delta\mu$
        - • Three cells
    - • Vocabulary from concluding factoids
- **BRAIN POWER**



FINIS

(except)