

Chemistry 163B

Lecture 25- Concluding Factoids W2013

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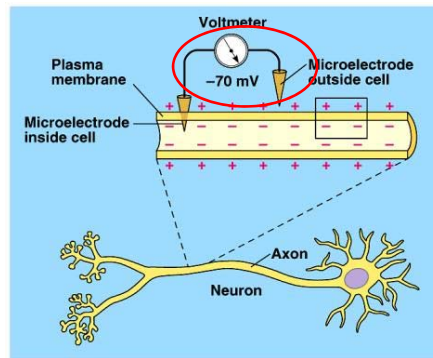
Concluding Factoids

and

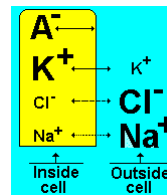
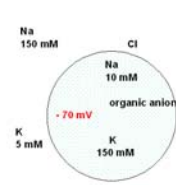
Comments

1

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

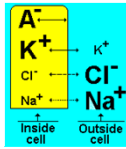
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resting potential and Nernst Equation

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 ⁺⁺)	0.1 μM	2 mM

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

$$\Phi^\circ = 0$$

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

$$\begin{aligned} \Phi &= -\frac{RT}{n\mathcal{F}} \ln Q = -0.02569 \ln \frac{[K^+]_{inside}}{[K^+]_{outside}} \\ &= -0.02569 \ln \frac{140 \text{ mM}}{5 \text{ mM}} = -0.086 \text{ V} \end{aligned}$$

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

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

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<http://www.cellbio.wustl.edu/faculty/huettemer/models.htm>

vocabulary

Gibbs-Duhem

the partial molar quantities do not vary independently

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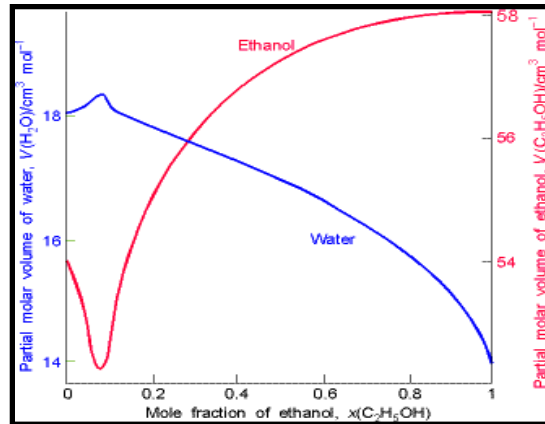
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Gibbs-Duhem

$$X_{\text{EtOH}} \left(\frac{\partial \bar{V}_{\text{EtOH}}}{\partial n_{\text{EtOH}}} \right)_{T,P,n_{\text{H}_2\text{O}}} = -X_{\text{H}_2\text{O}} \left(\frac{\partial \bar{V}_{\text{H}_2\text{O}}}{\partial n_{\text{EtOH}}} \right)_{T,P,n_{\text{H}_2\text{O}}}$$

what are
 $\left(\frac{\partial \bar{V}_a}{\partial n_a} \right)_{T,P,n_b}$ and $\left(\frac{\partial \bar{V}_b}{\partial n_a} \right)_{T,P,n_b}$
 when a and b
 form an ideal solution ?



do ideal
 solutions
 obey the
 Gibbs-Duhem
 relation?



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

non-ideal solutions

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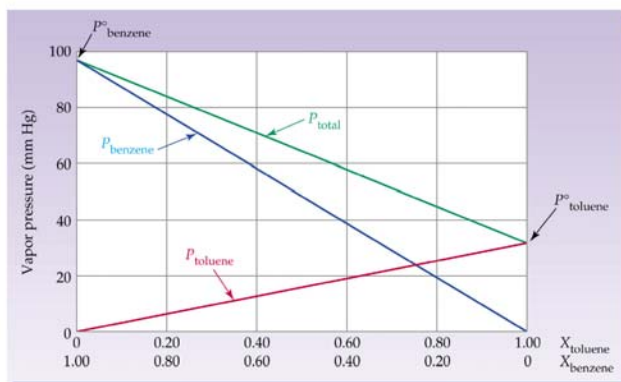
benzene-toluene, quite ideal (similar to Fig 9.2 E&R) !!

Raoult's Law of Ideal Solutions

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

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

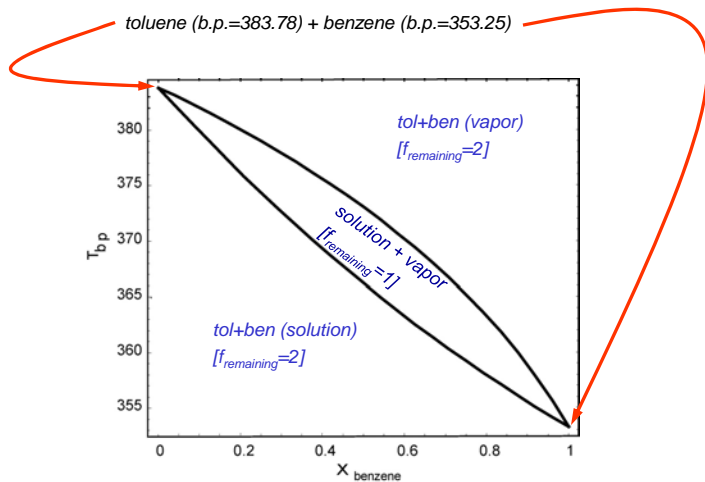
Benzene and Toluene



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

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



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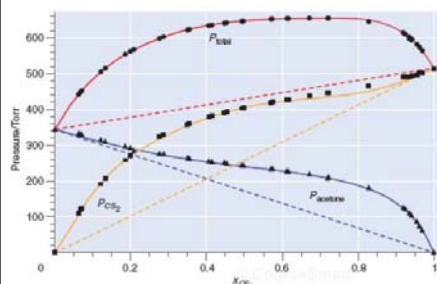
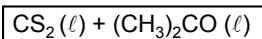
non-ideal solutions: azeotrope

Definition[s]:

- constant boiling liquid
- solution where the mole fraction of each component is the same in the liquid (solution) as the vapor
$$X_i^{(l)} = X_i^{(v)}$$
- boiling point of azeotrope may be higher or lower than of pure liquids

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



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

FIGURE 9.13

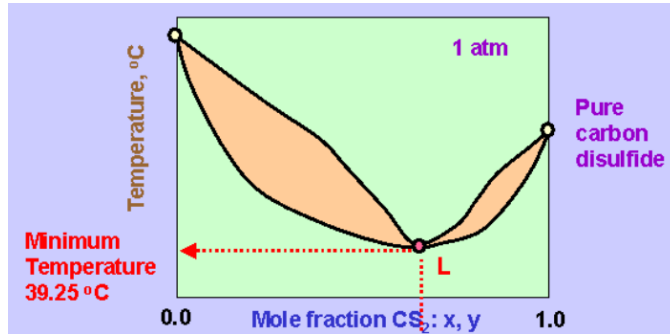
The data in Table 9.3 are plotted versus x_{CS_2} . The dashed lines show the expected behavior if Raoult's law were obeyed.

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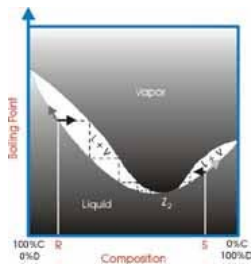
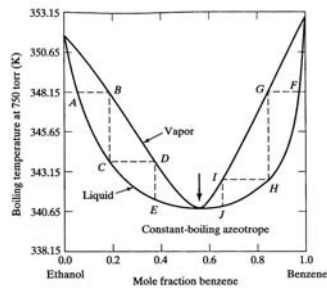
acetone-carbon disulfide: positive deviation \Rightarrow low boiling azeotrope



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

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low boiling azeotrope




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

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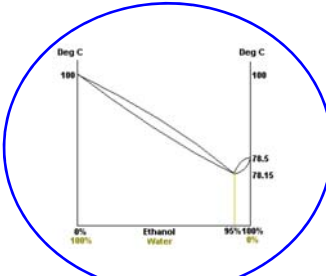
- weaker between component forces (A↔B) (than A ↔A, B ↔B)
- fractional distillation leads to constant boiling azeotrope in vapor
- and (in *pot* after azeotrope boils off)
 - $(X_A)_{\text{initial}} > (X_A)_{\text{azeotrope}}$ pure A
 - $(X_A)_{\text{initial}} < (X_A)_{\text{azeotrope}}$ pure B


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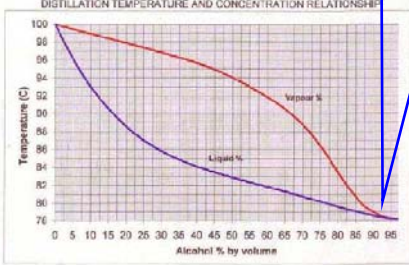


Water-Ethanol Mixture





DISTILLATION TEMPERATURE AND CONCENTRATION RELATIONSHIP:

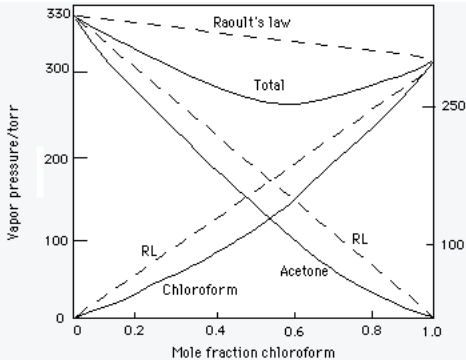


For the water-ethanol mixture, the azeotrope concentration corresponds to ~95% of ethanol in the mixture. This is the limit that can be reached by distillation of a less-alcohol-rich mixture.

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non-ideal solutions : negative deviations from ideal solution

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



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

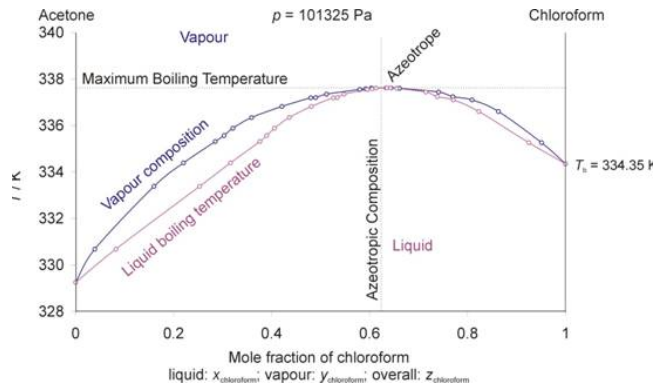
<http://dwb4.unl.edu/Chem/CHEM869W/CHEM869WImages/raoult2.gif>

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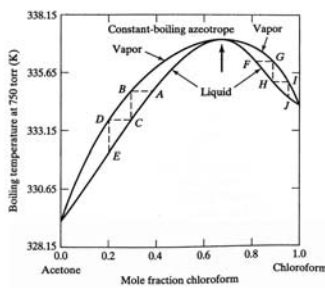
acetone-chloroform: negative deviation \Rightarrow high boiling azeotrope



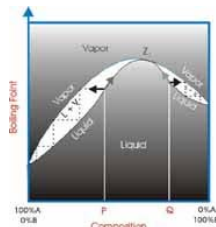
http://www.chm.bris.ac.uk/~chdms/Teaching/Chemical_Interactions/images/pic192.jpg

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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

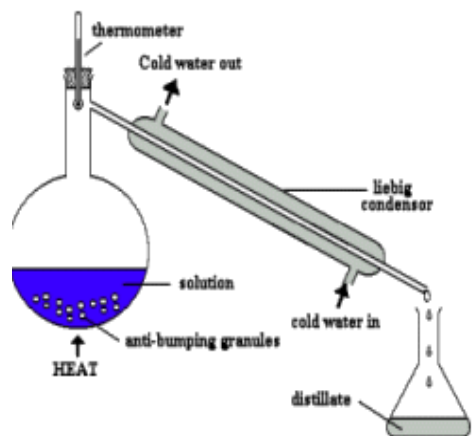
http://www.solvent--recycling.com/azeotrope_1.html

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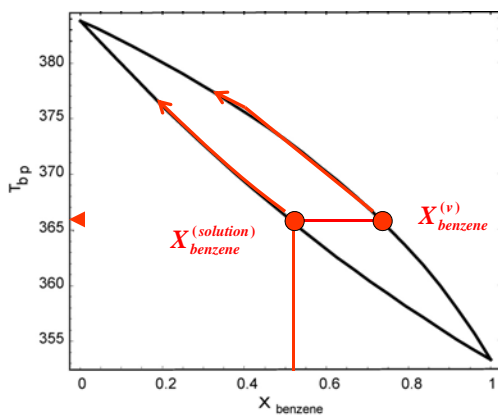
simple distillation



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

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



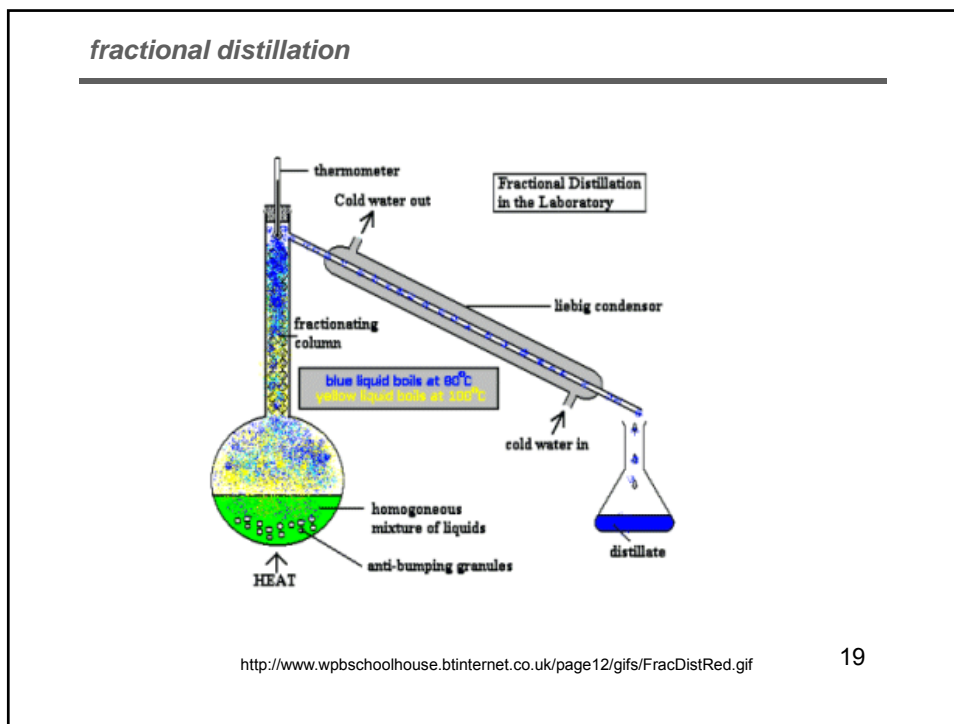
add heat
 $X_{benzene}^{(solution)}$ decreases
 T_{bp} increases gradually

$X_{benzene}$

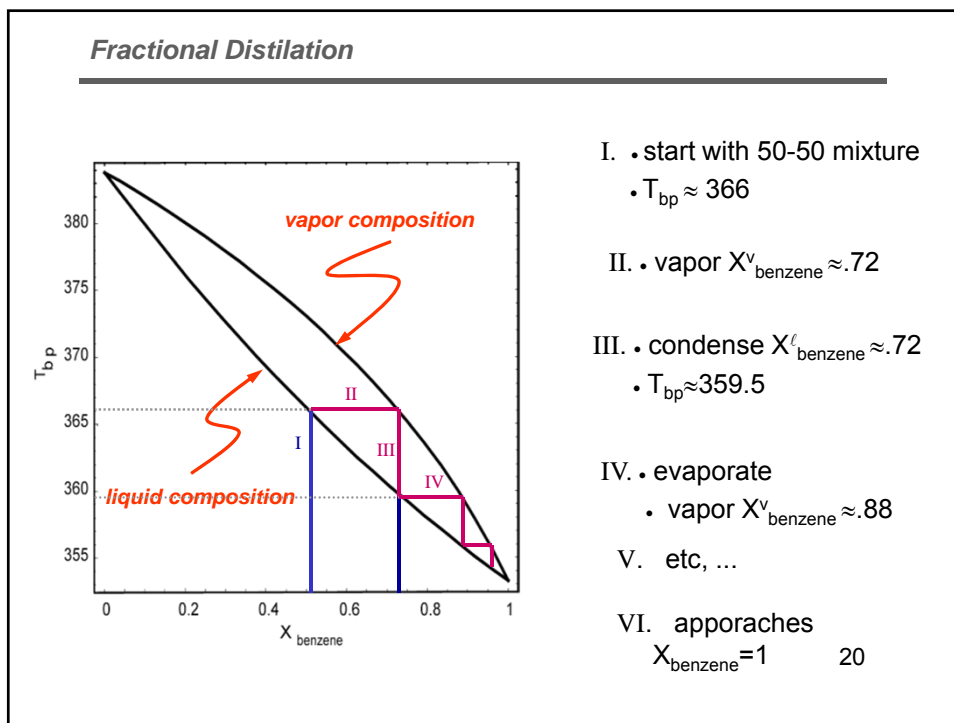
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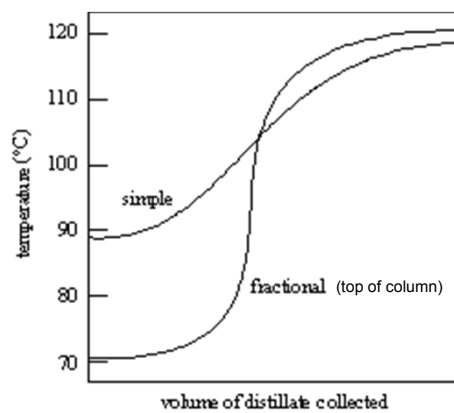
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T vs progress for a distillation



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

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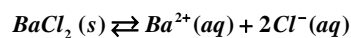
**Electrolytes and
Debye-Huckel Theory**

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activity coefficients for ions (HW8 #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 γ_{Cl^-} independently

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

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

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

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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

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

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]

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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]

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

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

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

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observations: thermo \equiv heat

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

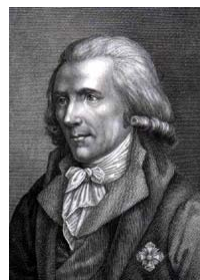
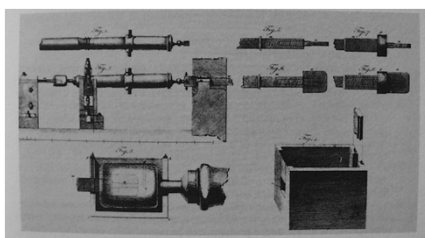


FIGURE 11. An illustration from Rumford's paper, "An Inquiry Concerning the Source of the Heat Which is Excited by Friction," showing the apparatus used by him in the cannon boring experiment. Figure 1, upper left, shows the cannon as received from the foundry, and Figure 2, below, shows it mounted in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

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1st law



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

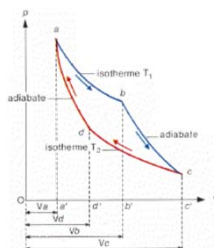
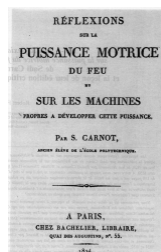
$$\oint dU = 0$$

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

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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



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

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

$$dS = \frac{dq_{\text{rev}}}{T}$$

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

$$\oint dS = 0$$

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

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

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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

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

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

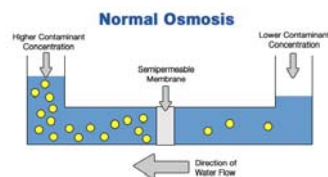
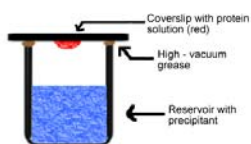
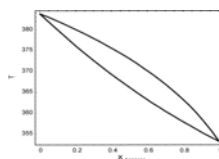
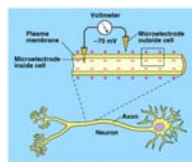
$$dG = -SdT + VdP + dw_{other}$$

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



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Applications



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quantitative-deductive mathematical abilities

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

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

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

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

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

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

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FINIS

(except)

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