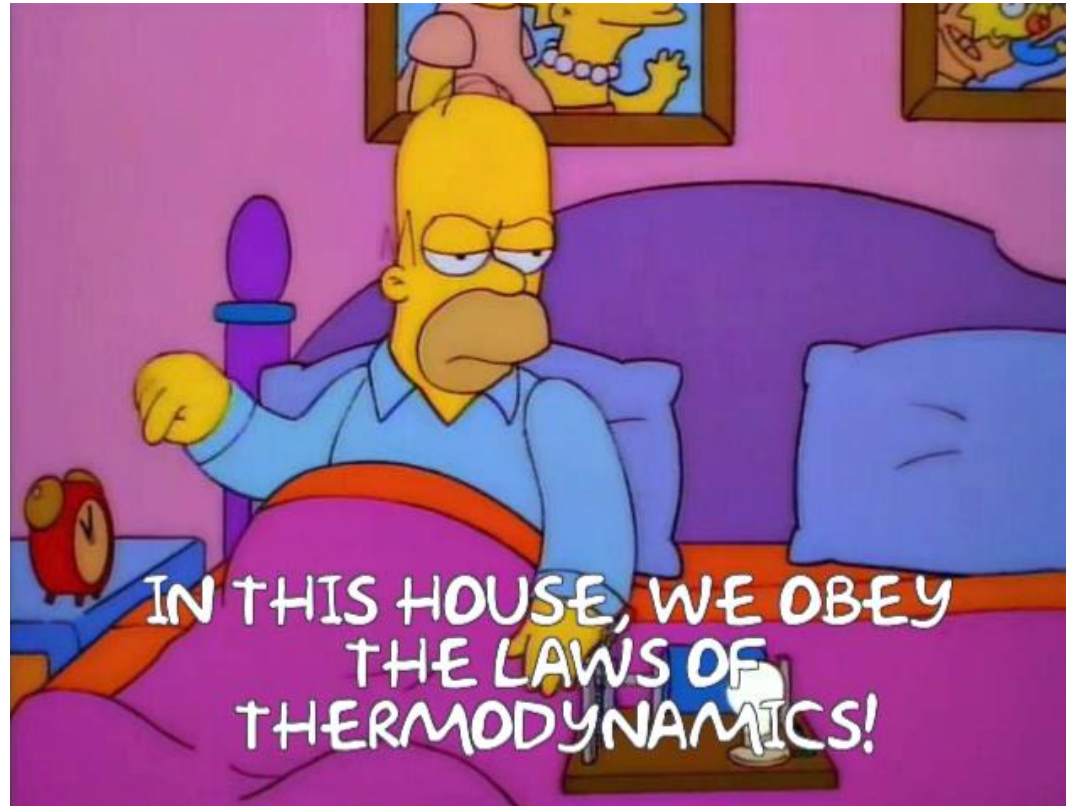


Thermodynamics (lecture 6)



Roel Dullens

Physics & Chemistry of Soft Matter

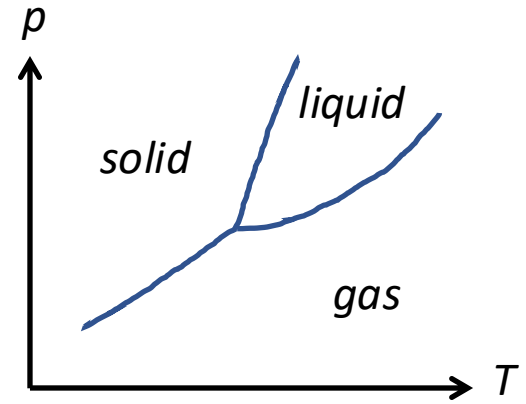
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Summary lecture 5

- Phase diagrams
 - Phase boundaries and their slopes
 - Clausius and Clausius-Clapeyron equations
- Chemical equilibrium
 - Reaction Gibbs energy
 - Equilibrium (at constant T and p)
 - Reaction quotient
 - Equilibrium constant

$$\frac{dp}{dT} = \frac{\Delta_{\text{trs}}S}{\Delta_{\text{trs}}V} = \frac{\Delta_{\text{trs}}H}{T\Delta_{\text{trs}}V}$$

$$\frac{d \ln p}{dT} = \frac{\Delta_{\text{trs}}H}{RT^2}$$



$$\Delta_r G \equiv \left(\frac{\partial G}{\partial \xi} \right)_{T,p} = \sum_i \nu_i \mu_i$$

$$\Delta_r G = 0$$

$$\Delta_r G = \Delta_r G^\ominus + RT \ln Q$$

$$\Delta_r G^\ominus = -RT \ln K_p \quad K_p = Q_{\text{eqm}} = \left[\prod_i \left(\frac{p_i}{p^\ominus} \right)^{\nu_i} \right]_{\text{eqm}}$$

Content of the course

- ✓ Introduction to Thermodynamics and gases
- ✓ The First Law of Thermodynamics
- ✓ Heat Capacities, Enthalpy and Thermochemistry
- ✓ The Second Law of Thermodynamics
- ✓ Helmholtz and Gibbs free energies
- ✓ Phase Transitions and Chemical Equilibrium
- **Chemical Equilibrium and Electrochemistry** → Today, lecture 6
- Ideal solutions, Colligative properties
- Condensation in the Van der Waals Equation of State

Today's lecture (6)

- Chemical equilibrium
 - Temperature dependence of K_p
 - Pressure dependence of composition
 - Generalisation: activity and activity coefficient
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 - Equilibrium of electrochemical cells
 - The Nernst equation and the equilibrium constant
 - Standard electrode potentials

from lecture 1:

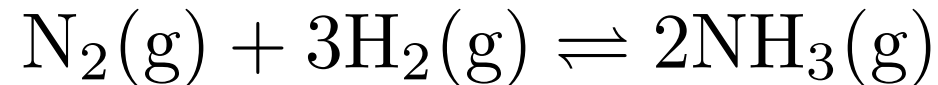
Le Chatelier's Principle

"A system at equilibrium will respond to a perturbation so as to relieve the effect of the perturbation"



Henry Louis Le Chatelier
(1850 – 1936)

1. Chemical reaction, e.g. Haber process



Thermodynamics:

- **calculate** the yield as function of T and p (lecture 6)
- tells us equilibrium position, but **nothing** about the rate

Temperature dependence of equilibrium constant K_p

$$\Delta_r G^\ominus = -RT \ln K_p$$

$$\left(\frac{\partial [G/T]}{\partial T} \right)_p = -\frac{H}{T^2}$$

$$\left(\frac{\partial \ln K_p}{\partial T} \right) = \frac{\Delta_r H^\ominus}{RT^2}$$

Van 't Hoff equation

For an endothermic reaction: $\Delta_r H^\ominus > 0 \rightarrow \frac{\partial \ln K_p}{\partial T} > 0$

- Increase in T : equilibrium shifts to the products (i.e. favours forward reaction)
- Consistent with Le Chatelier's principle (which does not apply to solids and liquids, see later)

Integrated Van 't Hoff equation

$$\ln \frac{K_2}{K_1} = -\frac{\Delta_r H^\ominus}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad \text{where} \quad K_i = K_p(T_i)$$

- Assumes $\Delta_r H^\ominus$ is independent of temperature
- What if $\Delta_r H^\ominus$ is not independent to temperature?

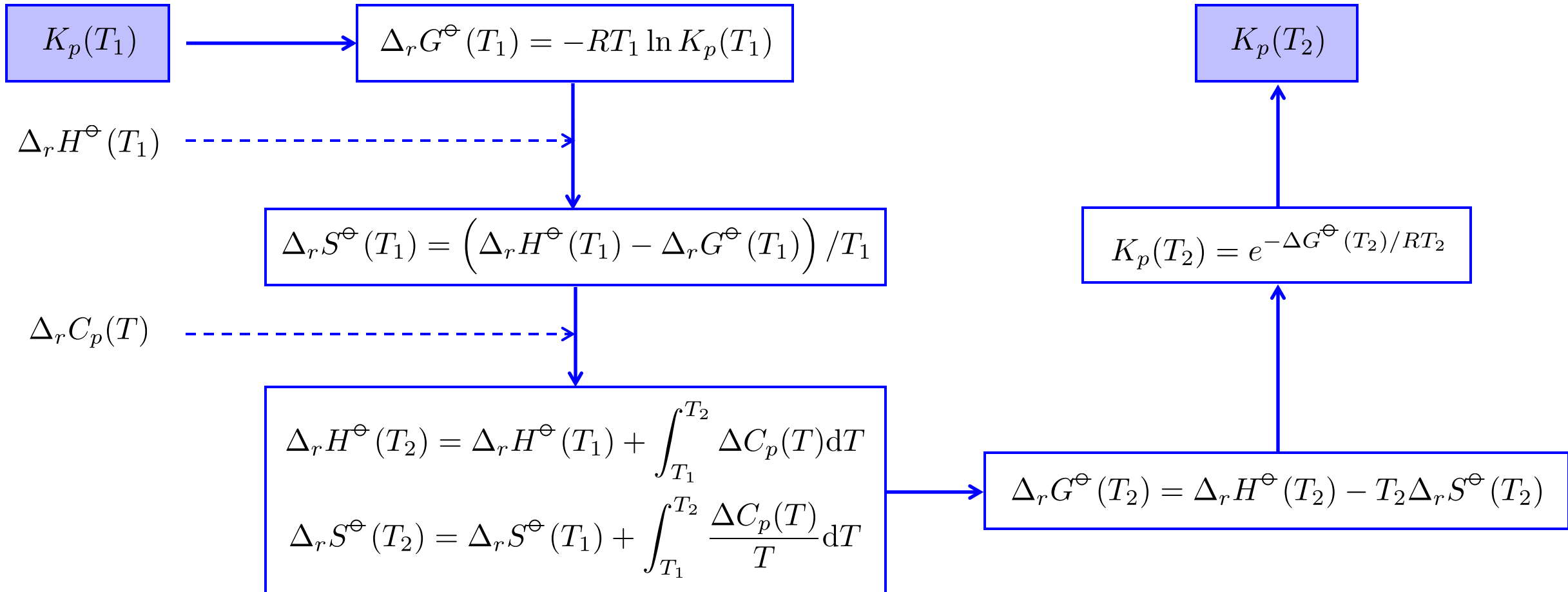


Longer, somewhat involved – but possible – calculation without approximations

Change of K_p with T if $\Delta_r H^\ominus$ is not independent of T

Longer, somewhat involved – but possible – calculation without approximations

Required knowledge:



Pressure dependence of equilibrium constant K_p

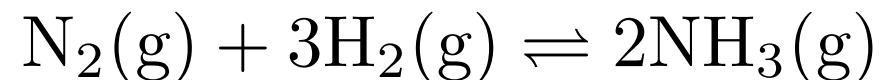
$$K_p = e^{-\Delta G^\ominus / RT} \quad \rightarrow \text{independent of pressure}$$



$$\left(\frac{\partial \ln K_p}{\partial p} \right)_T = 0$$

But **equilibrium position** (extent ξ or yield) **does** depend on pressure

Pressure dependence of equilibrium position

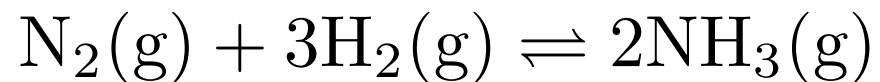


- Start with 1 mole of $\text{NH}_3(\text{g})$ in sealed container at constant T and p
- Assume all gases are perfect gases
- Equilibrium has been established
- We know (or calculate) $\Delta_r G^\ominus = \sum_i \nu_i \Delta_f G_{m,i}^\ominus$ ↗ tabulated for $T = 298 \text{ K}$
- And therefore $K_p = e^{-\Delta_r G^\ominus / RT}$

Calculate **equilibrium position** in terms of 'degree of dissociation' of NH_3 (α)

Note that α ($0 < \alpha < 1$) is a measure for the extent of the reaction ξ , BUT $\alpha \neq \xi$: $dn_i = \nu_i d\xi$

Pressure dependence of equilibrium position

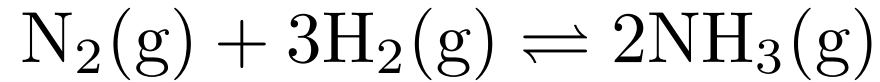


α : degree of dissociation of NH_3

By stoichiometry:

	$\text{N}_2(\text{g})$	$\text{H}_2(\text{g})$	$\text{NH}_3(\text{g})$	total
no. moles at start	0	0	1	1
no. moles at equilibrium	$\frac{1}{2}\alpha$	$\frac{3}{2}\alpha$	$1 - \alpha$	$1 + \alpha$
mole fractions (x_i)	$\frac{\frac{1}{2}\alpha}{1 + \alpha}$	$\frac{\frac{3}{2}\alpha}{1 + \alpha}$	$\frac{1 - \alpha}{1 + \alpha}$	1
partial pressures ($p_i = x_i p$)	$\frac{\frac{1}{2}\alpha}{1 + \alpha} p$	$\frac{\frac{3}{2}\alpha}{1 + \alpha} p$	$\frac{1 - \alpha}{1 + \alpha} p$	p

Equilibrium constant in terms of 'degree of dissociation'



$$K_p = \prod_i \left(\frac{p_i}{p^\ominus} \right)^{\nu_i} = \frac{\left(p_{\text{NH}_3} / p^\ominus \right)^2}{\left(p_{\text{N}_2} / p^\ominus \right) \left(p_{\text{H}_2} / p^\ominus \right)^3} = \dots = \frac{16}{27} \left(\frac{1 - \alpha^2}{\alpha^2} \right)^2 \left(\frac{p^\ominus}{p} \right)^2$$

DIY (do it yourself)

we know K_p ↓ calculate α (DIY)

Note that K_p depends on stoichiometry

- equilibrium position changes with stoichiometry
- So: be careful in Exercise 28: $\frac{1}{2}\text{N}_2(\text{g}) + \frac{3}{2}\text{H}_2(\text{g}) \rightleftharpoons \text{NH}_3(\text{g})$

$$\alpha = \sqrt{\frac{1}{1 + \sqrt{\frac{27K_p}{16}} \left(\frac{p}{p^\ominus} \right)}}$$

equilibrium composition

Today's lecture (6)

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 - **Generalisation: activity and activity coefficient**
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Generalisation: activity and activity coefficient

So far, only considered reactions involving *perfect gases*

Chemical potential

$$\mu_i = \mu_i^\ominus + RT \ln \frac{p_i}{p^\ominus}$$



Equilibrium constant

$$K_p = \prod_i \left(\frac{p_i}{p^\ominus} \right)^{\nu_i}$$

... all in terms of partial pressures (of the perfect gases) ...

More generally, write equations in terms of *activities* a_i

$$\mu_i = \mu_i^\ominus + RT \ln a_i$$



$$K_p = \prod_i a_i^{\nu_i}$$

- a_i is the *activity of component i* (dimensionless)
- Defined for all different states (gases, solids, liquids, solutions, ...)

Activity and activity coefficients for different states

- Perfect gases $a_i = \frac{p_i}{p^\ominus}$ p_i : partial pressure, with $p^\ominus = 1 \text{ bar}$ (as we have used so far)
-

- Real gases $a_i = \gamma_i \frac{p_i}{p^\ominus}$ γ_i : activity coefficient → accounts for deviations from 'ideality'
 $\gamma_i = 1$ for perfect gas
-

- Solutions $a_i = \gamma_i x_i$ x_i : mole fraction (as seen before)
 $\gamma_i = 1$ for ideal solutions (see lecture 7)

$$a_i = \gamma_i \frac{c_i}{c^\ominus}$$

c_i : molarity with $c^\ominus = 1 \text{ mol dm}^{-3}$

$$a_i = \gamma_i \frac{b_i}{b^\ominus}$$

b_i : molality with $b^\ominus = 1 \text{ mol kg}^{-1}$

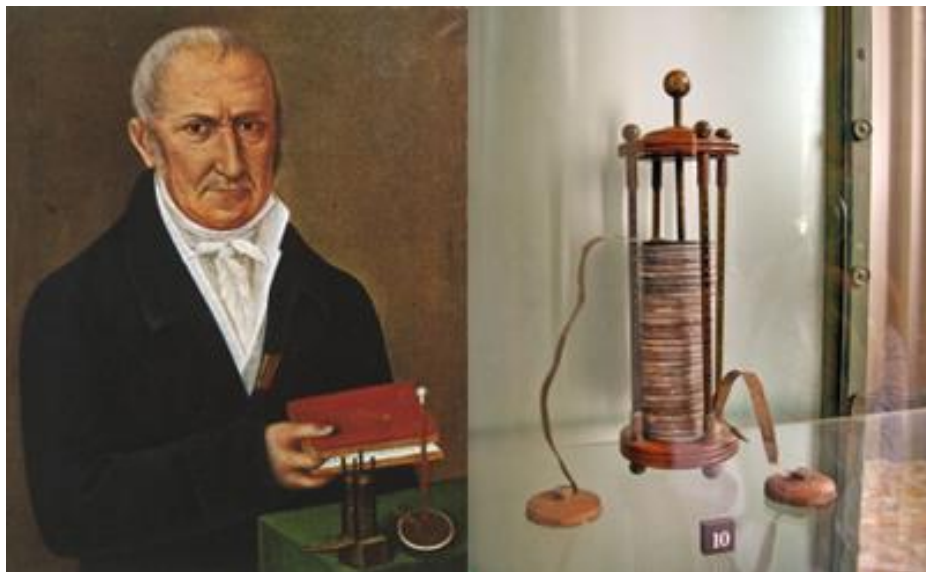
- Solids and liquids $a_i = 1$ This is why Le Chatelier's principle does not apply to solids and liquids: no contribution to $K_p = \prod_i a_i^{\nu_i}$

Today's lecture (6)

- Chemical equilibrium
 - Temperature dependence of K_p
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- **Electrochemistry**
 - Electrochemical cells, the cell potential and cell reactions
 - Equilibrium of electrochemical cells
 - The Nernst equation and the equilibrium constant
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Electrochemistry: connecting chemistry and electricity

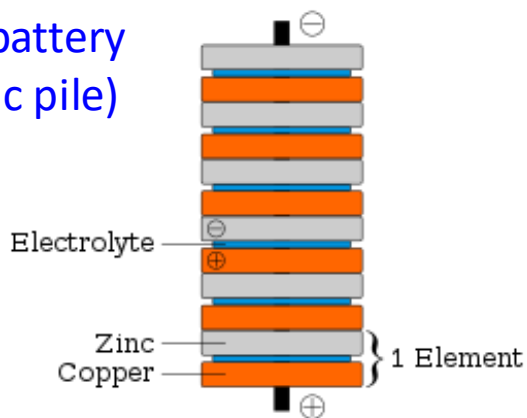
The first battery



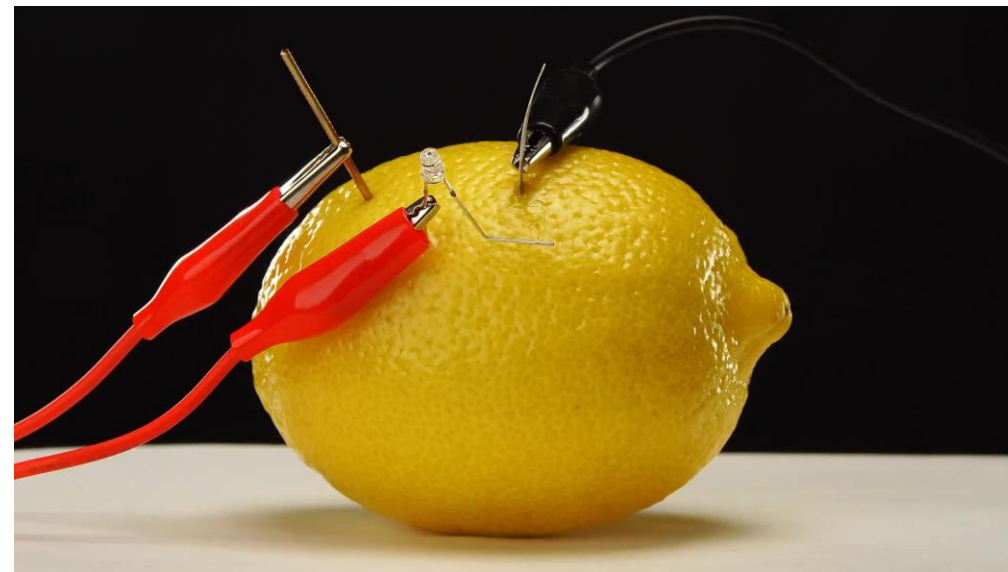
Alessandro Volta
(1745 -1827)

Volta battery
(voltaic pile)

Cardboard soaked in salt water

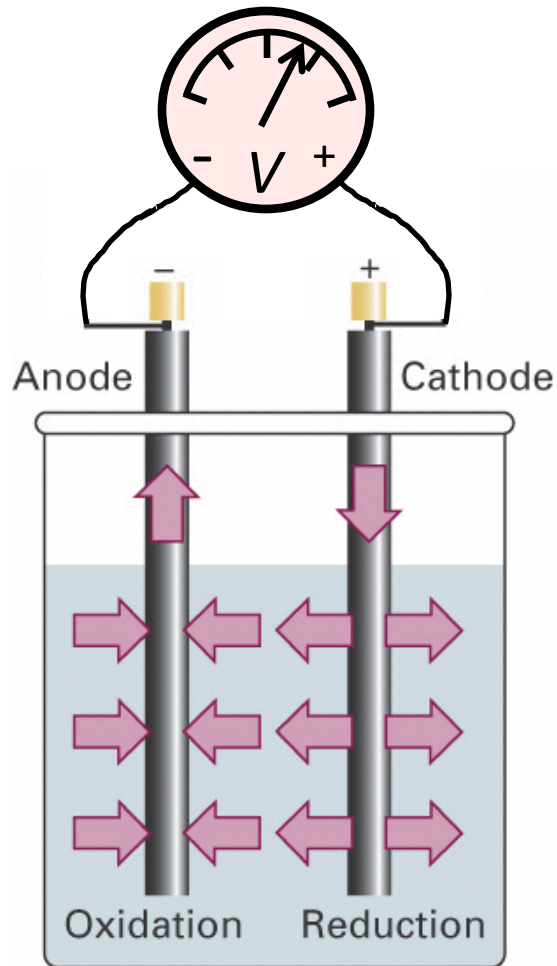


Your own (fruit) battery?



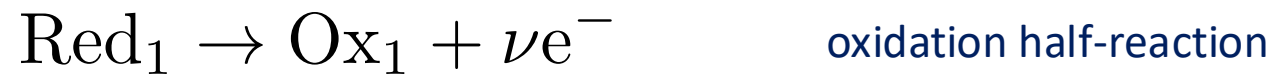
Lemon battery

Electrochemical cells and the cell potential E_{cell}



Redox reaction: reaction in which there is a transfer of e^-

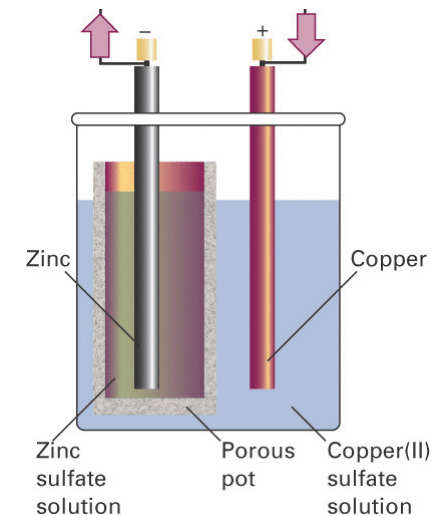
- Consists of two half-reactions: oxidation and reduction
- Oxidizing agent (oxidant, Ox): electron acceptor
- Reducing agent (reductant, Red): electron donor



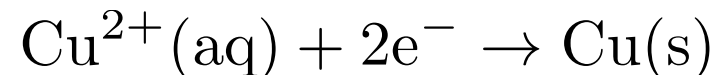
An electrochemical cell has a cell potential E_{cell}

- The potential *difference* between the electrodes
- E_{cell} is measured in voltage (V)

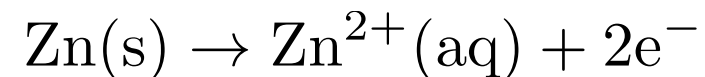
Cell reactions – the ‘Daniel’ cell



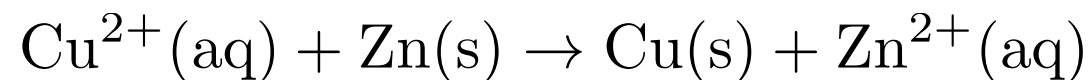
RHS: cathode → reduction of oxidizing agent:



LHS: anode → oxidation of reducing agent:



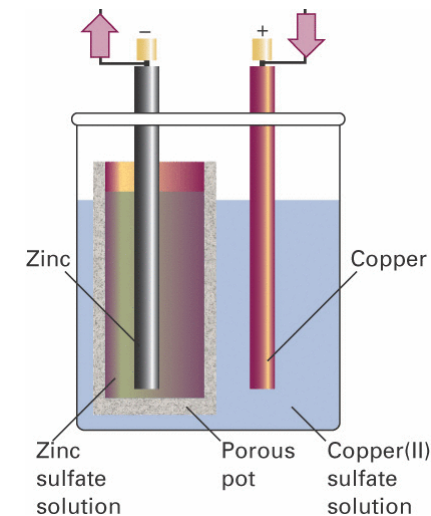
Cell reaction:



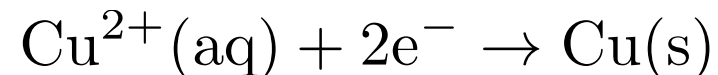
Cell reactions – alternative strategy



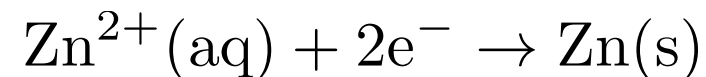
Write everything in terms of reduction half-reactions



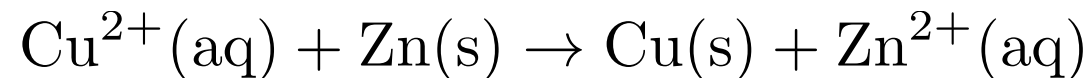
RHS: reduction of oxidizing agent written as reduction:



LHS: oxidation of reducing agent, written as reduction:

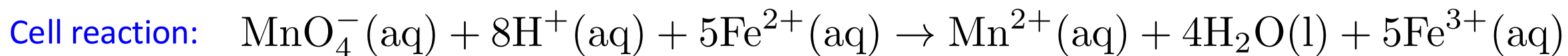
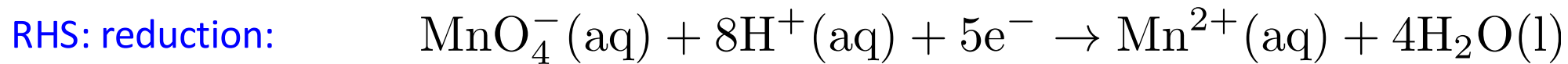


Cell reaction = RHS – LHS:



- Be clear on which 'approach' you use
- Balance the ve^{-} of both half reactions

Example



Standard
reduction
potentials!

$$E_{\text{RHS}}^{\ominus} = +1.51 \text{ V}$$

$$E_{\text{LHS}}^{\ominus} = +0.77 \text{ V}$$

+

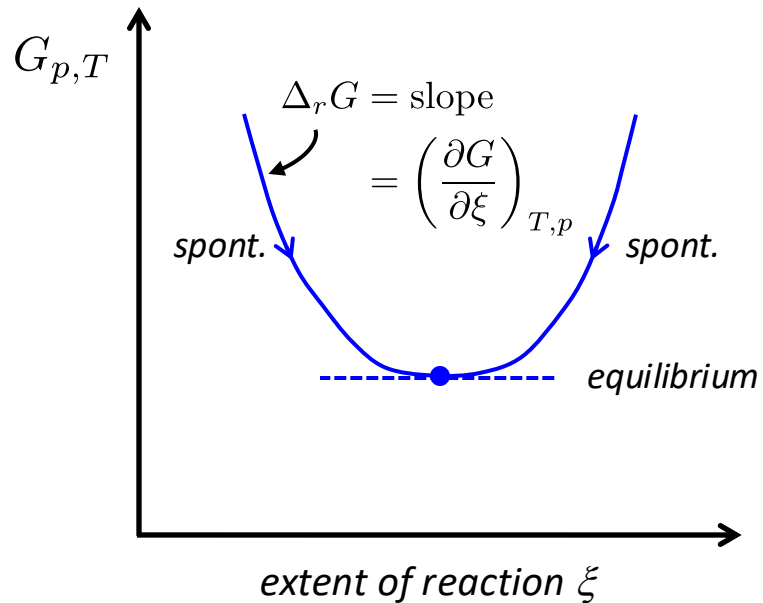
Standard cell potential: $E_{\text{cell}}^{\ominus} = E_{\text{RHS}}^{\ominus} - E_{\text{LHS}}^{\ominus} = 1.51 - 0.77 = 0.74 \text{ V}$

Today's lecture (6)

- Chemical equilibrium
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 - **Equilibrium of electrochemical cells**
 - The Nernst equation and the equilibrium constant
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Equilibrium of electrochemical reactions

Recall from lecture 5:

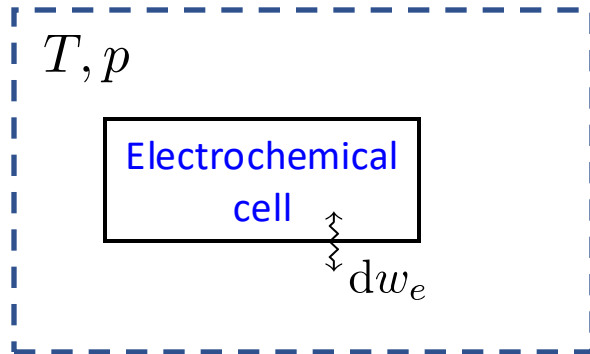


$$\Delta_r G \equiv \left(\frac{\partial G}{\partial \xi}\right)_{T,p}$$

- $\Delta_r G < 0$: forward reaction ($\xi \uparrow$) spontaneous
- $\Delta_r G > 0$: backward reaction ($\xi \downarrow$) spontaneous
- $\Delta_r G = 0$: **equilibrium**

We need to relate $\Delta_r G$ to the cell potential E_{cell}

Relation between $\Delta_r G$ and the cell potential E_{cell}



- Closed system and additional electrical work

$$dw_{\text{rev}} = -pdV + \phi dQ$$

- Here: $\phi = E_{\text{cell}}$
- Faraday's constant: $F = eN_{AV}$

Fundamental equation for Gibbs free energy:

$$dG = -SdT + Vdp + \phi dQ$$



$$\Delta_r G \equiv \left(\frac{\partial G}{\partial \xi} \right)_{T,p}$$

$$\Delta_r G = -\nu F E_{\text{cell}}$$

The key link between electrical measurements and thermodynamic properties!

The Nernst equation

Recall from lecture 5:

$$\Delta_r G = \Delta_r G^\ominus + RT \ln Q$$



$$\Delta_r G = -\nu F E_{\text{cell}}$$

Nernst equation

$$E_{\text{cell}} = E_{\text{cell}}^\ominus - \frac{RT}{\nu F} \ln Q$$

Reaction quotient

$$Q = \prod_i a_i^{\nu_i}$$

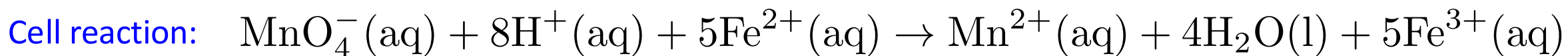
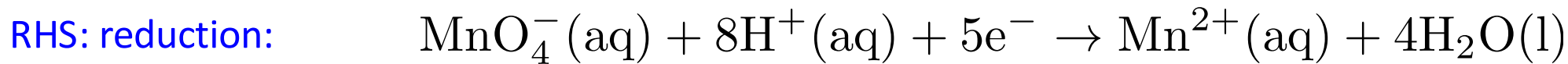
Standard cell potential

$$\Delta_r G^\ominus = -\nu F E_{\text{cell}}^\ominus$$

If all reactants and products are in their standard states ($a_i = 1$)

$$E_{\text{cell}} = E_{\text{cell}}^\ominus \quad (Q = 1 \rightarrow \ln Q = 0)$$

Same example again



Standard
reduction
potentials!

$$E_{\text{RHS}}^{\ominus} = +1.51 \text{ V}$$

$$E_{\text{LHS}}^{\ominus} = +0.77 \text{ V}$$

+

Nernst equation:

$$E_{\text{cell}} = E_{\text{cell}}^{\ominus} - \frac{RT}{5F} \ln \frac{(a_{\text{Mn}^{2+}})(a_{\text{H}_2\text{O}})^4(a_{\text{Fe}^{3+}})^5}{(a_{\text{MnO}_4^-})(a_{\text{H}^+})^8(a_{\text{Fe}^{2+}})^5}$$

Equilibrium in electrochemical cells

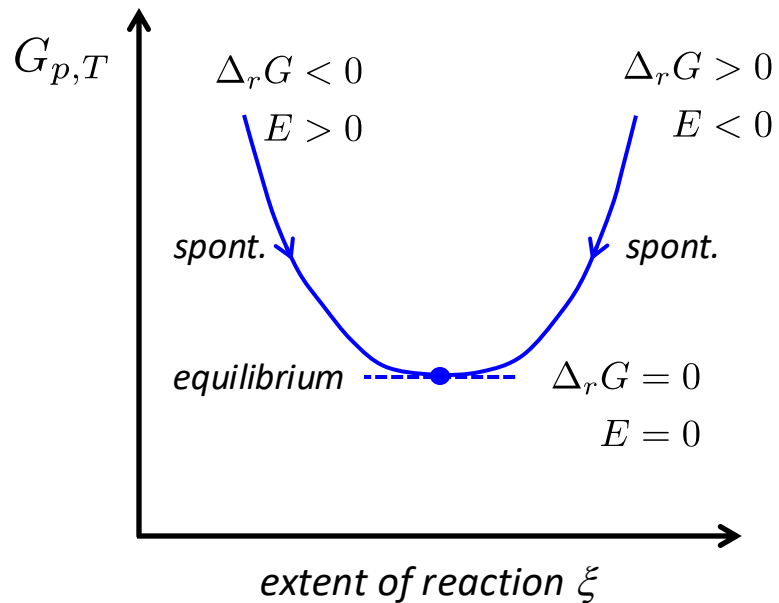
$\Delta_r G = 0$: equilibrium

$$\Delta_r G = -\nu F E_{\text{cell}}$$

$E_{\text{cell}} = 0$: equilibrium

$$E_{\text{cell}}^{\ominus} = \frac{RT}{\nu F} \ln K_p$$

(compare : $\Delta_r G^{\ominus} = -RT \ln K_p$)



- $\Delta_r G < 0$ or $E_{\text{cell}} > 0$: forward reaction ($\xi \uparrow$) spontaneous
- $\Delta_r G > 0$ or $E_{\text{cell}} < 0$: backward reaction ($\xi \downarrow$) spontaneous
- $\Delta_r G = 0$ or $E_{\text{cell}} = 0$: equilibrium

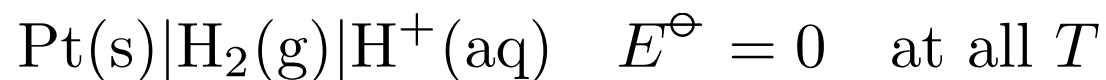
Relation between $\Delta_r S^\ominus$ and $\Delta_r H^\ominus$ and E_{cell}^\ominus

$$\begin{array}{ccc} \Delta_r G^\ominus = -\nu F E_{\text{cell}}^\ominus & & \\ \downarrow S = -\left(\frac{\partial G}{\partial T}\right)_p & \xrightarrow[\text{constant } T]{G = H - TS} & \Delta_r H^\ominus = -\nu F \left(E_{\text{cell}}^\ominus - T \frac{dE_{\text{cell}}^\ominus}{dT} \right) \\ \Delta_r S^\ominus = \nu F \frac{dE_{\text{cell}}^\ominus}{dT} & & \boxed{\Delta_r G = -\nu F E_{\text{cell}}} \end{array}$$

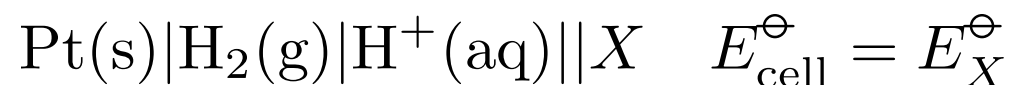
***The key link between electrical measurements
and thermodynamic properties!***

Standard electrode potentials

“Zero-reference electrode”: *Standard hydrogen electrode*:



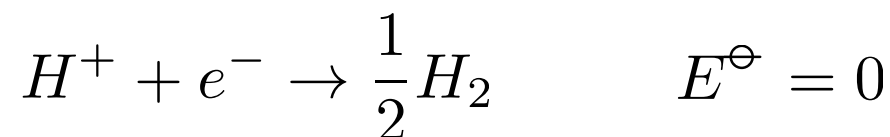
Standard electrode potential of redox-couple X:



RHS: reduction of redox couple X, written as reduction:



LHS: oxidation of hydrogen, **BUT written as reduction**:

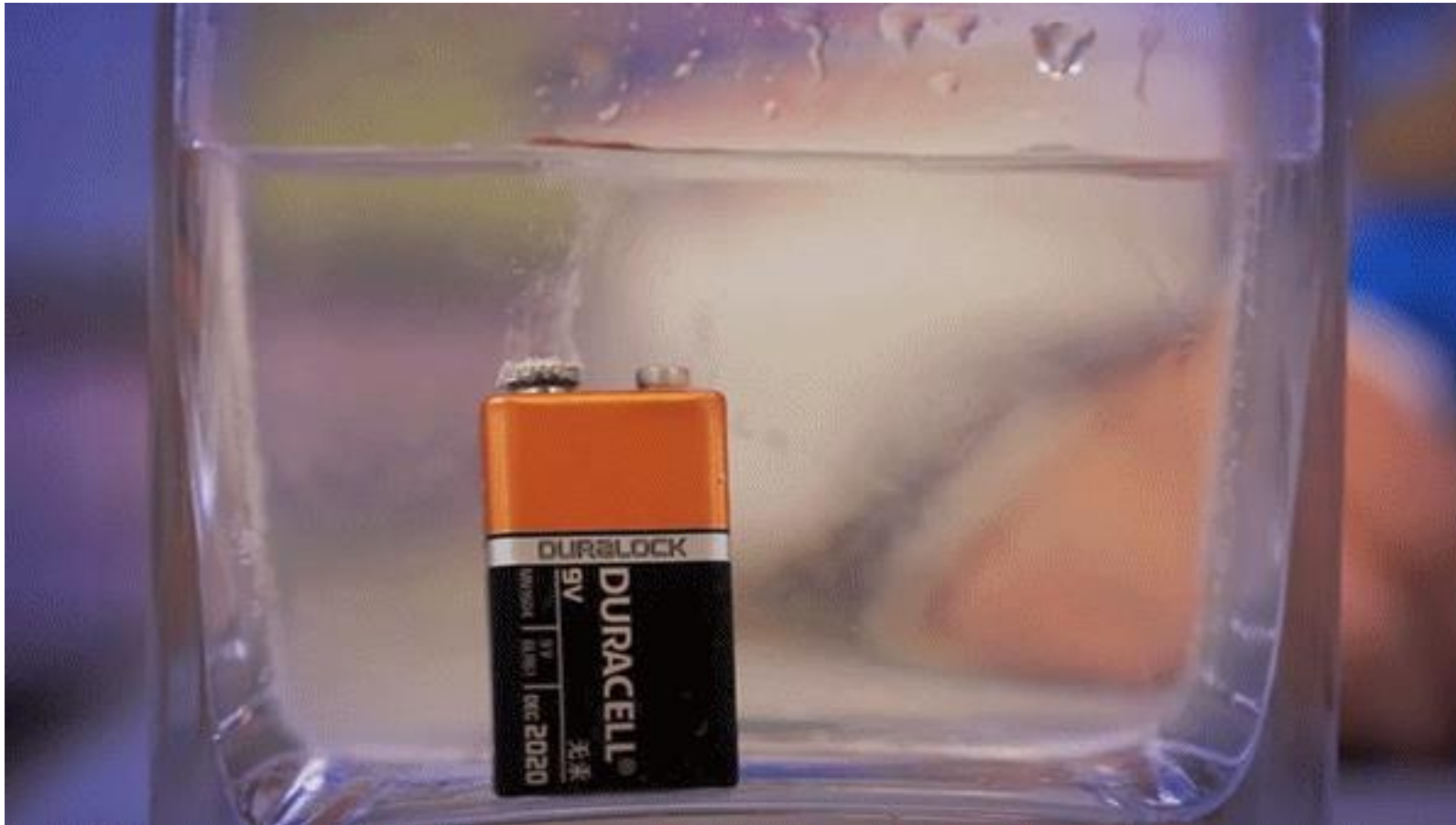


$$E_{\text{cell}}^\ominus = E_{\text{RHS}}^\ominus - E_{\text{LHS}}^\ominus = E_X^\ominus - 0 = E_X^\ominus$$

tabulated for $T = 298 \text{ K}$

And now for something completely different ...

Electrolysis of water



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 - ✓ Chemical Equilibrium and Electrochemistry
 - Ideal solutions, Colligative properties
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- } lecture 7