CHEM 206 section 01

LECTURE #10 Wed. Feb.06, 2008

LECTURE TOPICS:

TODAY'S CLASS: finish Ch.14.4
start Ch.15

NEXT CLASS: continue Ch.15

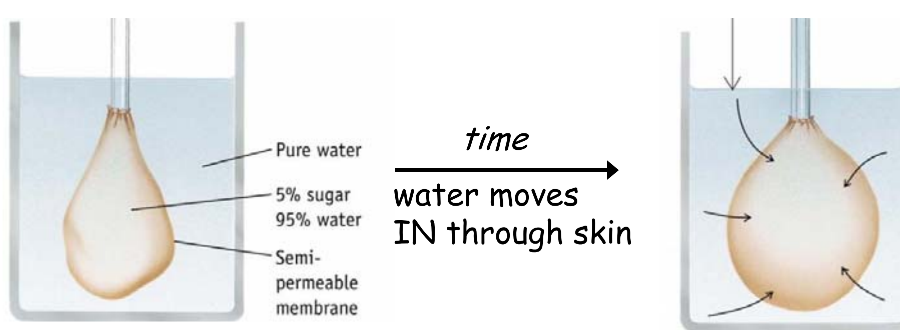
(1)

14.4 Colligative properties: Osmotic Pressure

Q: Ever forgotten grapes in water while washing them??
(EVENTUALLY, THEY BURST...)

Inside grape:
lots of sugars, salts...

→ pressure
builds up!



Modified K&T Fig.14.14

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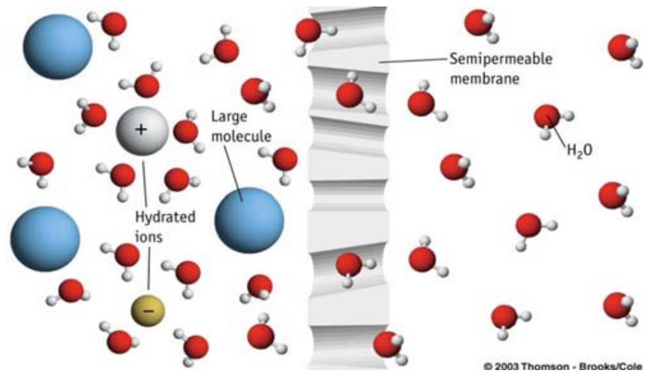
K&T
Fig.14.15

Osmosis
at the
particulate
level



Osmosis = net flow of solvent through a semipermeable membrane, down its concentration gradient

WHAT IS HAPPENING: all molecules bump into membrane…
…but only solvent can pass through

THUS: side with more water molecules has higher frequency of water molecules "escaping" to other side

NET FLOW: solvent moves to where there is less solvent
***i.e.,* to where there is more solute**

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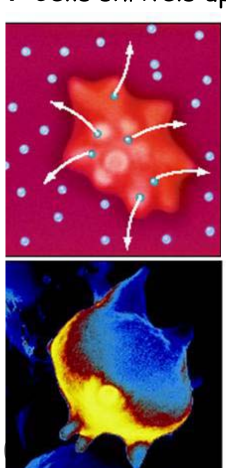
Why *not just any solution* should be injected into the blood…

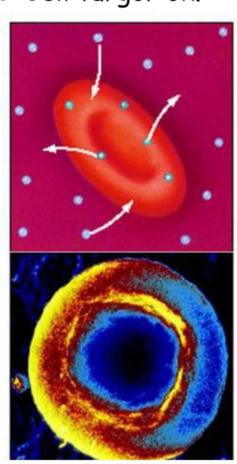
Hypertonic solution
[solute] greater than
inside cells
→ Water flows out
→ Cells shrivels up



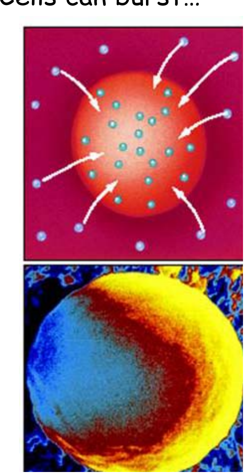
K&T
Figure
14.16

RED
BLOOD
CELLS

Isotonic solution
[solute] same as
inside cells
→ "isoosmotic"
→ No net osmosis
→ Cell turgor ok.

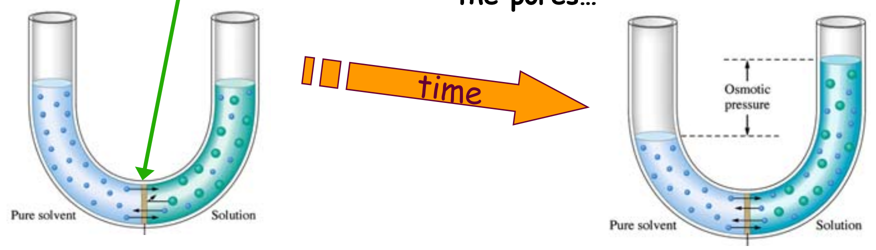


Hypotonic solution
[solute] less than
inside cells
→ Water flows in
→ Cells can burst…



Quantitation: Solutions exert osmotic pressure

SEMIPERMEABLE MEMBRANE: solvent molecules can pass through the pores…



Initially: net flow into sol'n

Driving force = concentration of solvent higher on one side

Zumdahl's Figure 11.18

•At equilibrium: no net flow rate of solvent transfer is equal in both directions

Concentration gradient is COUNTERED BY: pressure exerted by higher column of liquid on one side

Osmotic Pressure = The excess 'hydrostatic' pressure on the solution compared to the pure solvent.

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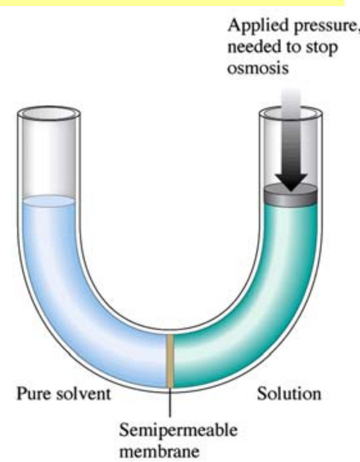
Osmometry: OSMOTIC PRESSURE CAN BE MEASURED VERY ACCURATELY & LETS US DETERMINE SOLUTE CONCENTRATION

Zumdahl's Figure 11.17

FLOW DUE TO OSMOSIS can be prevented by APPLYING EXTERNAL PRESSURE



minimum P_{ext} required to stop flow = solution's **osmotic pressure**, Π
a capital "pi"

To relate this to the TOTAL CONCENTRATION OF SOLUTE PARTICLES (don't forget i where necessary):

same form as the ideal gas law:

$\Pi V = nRT$ *or* $\Pi = cRT$

Use osmometry to identify this unknown:

A 25.00 mL solution containing 4.562 mg of an unidentified ionic compound with formula MCl_3 exhibits an osmotic pressure of 83.1 ± 0.6 mm Hg at 22°C. What is the likely identity of "M"?

1st: assumption required: ions fully dissociated in solution (i = 4)

① Use osmotic P to find n_{solute} = total # moles of dissolved ions!

$$\Rightarrow n_{ions} = \Pi V/RT = \frac{(83.1 \text{ mm Hg})}{(760 \text{ mm Hg}\cdot\text{atm}^{-1})} \times \frac{(0.02500 \text{ L})}{(0.08206 \text{ Latm}\cdot\text{mol}^{-1}\text{K}^{-1})(295\text{K})}$$

$= 1.129\times10^{-4}$ mol of ions *(1 extra SF)*

② Find MM: must remember where the ions came from…

4 ions per MCl_3 unit $\Rightarrow n_{MCl3} = n_{ions}/4 = 2.823\times10^{-5}$ mol MCl_3

$MM_{MCl3} = (0.004562 \text{ g}) / (2.823\times10^{-5} \text{ mol})$
$= 161.6$ g/mol *(1 extra SF)* ← **MM = link to identifying M!**

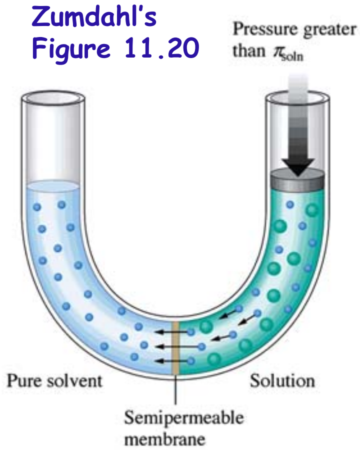
$MM_{MCl3} = MM_M + 3MM_{Cl} \Rightarrow MM_M = MM_{MCl3} - 3MM_{Cl}$
$= 161.6 - (3\times35.45)$
$= 55.3$ g/mol *(3 SF…)*

% error in Π = 100x(0.6/83.1) = 0.72%
If % error in MM_M is same: $55.3 \pm (0.0072\times55.3) = 55.3 \pm 0.4$ g/mol
Close to Mn (54.94 g/mol) & Fe (55.85 g/mol); cannot conclude which…

REVERSE OSMOSIS: *like molecular-level filtration*

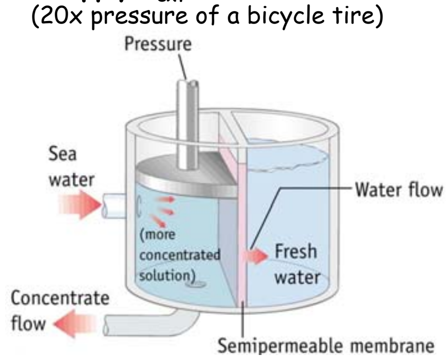
If the external pressure is larger than the osmotic pressure, **reverse osmosis** occurs ⇨ solvent flows OUT of the solution.

Zumdahl's Figure 11.20



Desalination of sea water:

35g of salts per kg sea water
⇨ Π = 27 atm for sea water
⇨ reverse osmosis works well if apply P_{ext} = 50 atm
(20x pressure of a bicycle tire)



K&T's A Closer Look, p.585

Summary: Colligative Properties of Solutions

	Pure solvent	Solution (= solvent + solute)	
Vapour pressure	P^o (characteristic)	$P_{soln} = \chi_{solvent} P^o_{solvent}$	*Volatile fraction?* *additive if > 1 volatile*
Boiling point	b.p. (characteristic) K_b (characteristic)	$\Delta T_{bp} = K_b\, m_{solute}$	*Total solute molality?* *include van't Hoff factor **i***
Freezing point	m.p. (characteristic) K_f (characteristic)	$\Delta T_{fp} = K_f\, m_{solute}$	*Total solute molality?* *include van't Hoff factor **i***
Osmotic pressure	does not exert osmotic pressure	$\pi = \left(\frac{n_{solute}}{V_{solute}}\right) RT$	*Total solute <u>molarity</u>?* *include van't Hoff factor **i***

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Chapter 15: CHEMICAL KINETICS

= the area of chemistry concerned with rxn rates

- Rxn may be spontaneous…but will it occur in our lifetime?
  - Diamond → graphite…
- Exothermic rxns: will heat be generated faster than we can dissipate it?
- How long until this radioactive sample will be safe?
- Will a reaction take 5 min, an hour, or a week?

Chapter Outline

15.1 Rates of chemical reactions
15.2 Reaction conditions & rate
15.3 Effect of concentration on reaction rate
15.4 Concentration-time relationships: Integrated rate laws
15.5 Particulate view of rxn rates
15.6 Reaction mechanisms

Chapter Goals

- **Understand rates of rxns & conditions affecting rates**
- **Derive rate equation (rate law), rate constant & reaction order from experimental data**
- **Use integrated rate laws**
- **Understand collision theory & role of activation energy**
- **Relate rxn mechanisms & rate laws**

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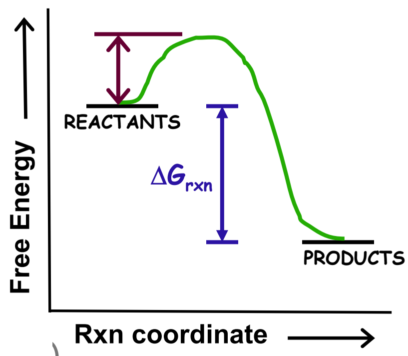
Kinetics vs. Thermodynamics

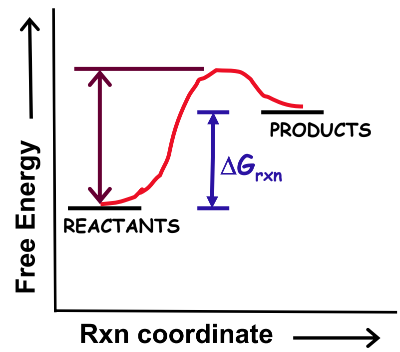
Thermodynamically favourable (exergonic) processes

- *Should* yield products… *BUT…*
- Rate depends on how many molecules can "get over" the activation barrier
- So, might be very very slow…

Thermodynamically unfavourable (endergonic) processes

- Often large activation barriers
- Typically very slow fwd reaction at room temperature





Summary of chem206 attack plan for KINETICS

KINETICS

- <u>Will</u> this really happen?
  - How fast is the process?
- What barriers must be overcome?

Pathway is crucial !

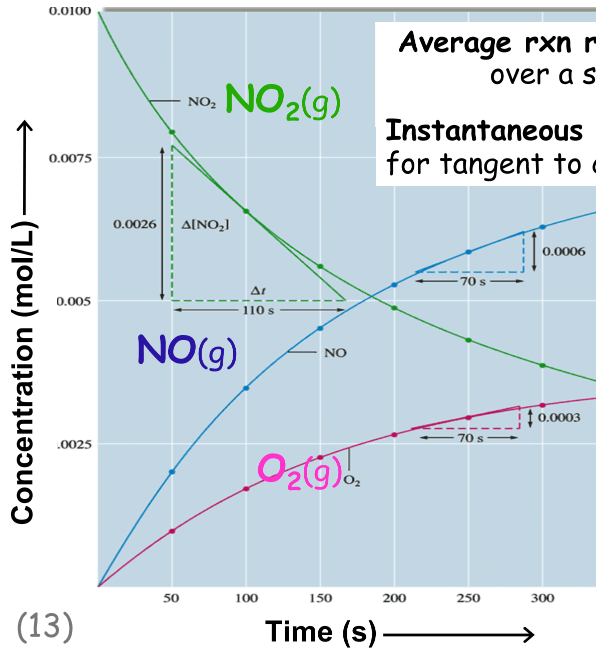
- How does it happen?
- One step or many steps?
- Which step is slowest?
- Relative energies of intermediate "states" are IMPORTANT

- Rxn rates – definitions
- Rates depend on conc'ns
- Exp'ts to probe this…

- Temp. affects collisions!
- Collision theory
- Activation energy

- Learning mechanistic info. from exp'tal rate data (CONNECTS TO 1ST PART)
- How to speed up a rxn (catalysis)

Consider RXN: $NO_2(g) \rightarrow NO(g) + \frac{1}{2}\, O_2(g)$



Average rxn rate: slope calculated over a specified time period

Instantaneous rate: slope calculated for tangent to curve (or *very* short Δt)

NO_2 disappears at same rate that NO appears…

…but what is the relative rate of appearance of O_2?

Zumdahl's Fig.12.1
similar: K&T Fig.15.2

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15.1 Reaction Rates: how fast do [ ]'s change?

RATE = Change in concentration of a reactant or product per unit time

COMMON SENSE:

as rxn proceeds, [reactants] ↓ and [products] ↑

$$\text{RATE} = -\frac{\Delta[\text{reactant}]}{\Delta t}$$

Reactants disappearing…
…so Δ[reactant] is NEGATIVE
Add "-" sign ⇒ RATE is positive

$$\text{RATE} = +\frac{\Delta[\text{PRODUCTS}]}{\Delta t}$$

Products appearing…
…so Δ[product] is POSITIVE
⇒ RATE is positive

Must specify exactly which species you are talking about…

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Summarizing rate expressions

For a given reaction, to equate rxn rates according to different reactant/product species analyzed: **"normalize"**

Divide $\frac{\Delta[\text{species}]}{\Delta t}$ by the stoichiometric coefficient for that species in the balanced rxn eqn

Example: for rxn $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$

$$\text{Rxn rate} = -\frac{1}{2}\frac{\Delta[N_2O_5]}{\Delta t} = +\frac{1}{4}\frac{\Delta[NO_2]}{\Delta t} = +\frac{\Delta[O_2]}{\Delta t}$$

Note: specify that you have presented a "normalized" reaction rate

Why?

- not a fixed convention
- many people just specify which substance used to determine rate

Consider some reactions involved in ozone destruction…

Ozone depletion summarized: http://nobelprize.org/chemistry/laureates/1995/press.html

Chlorine monoxide plays a major role in the creation of the ozone holes in the stratosphere over Earth's polar regions. ClO itself forms in the stratosphere when ozone reacts with Cl_2 (largely formed via UV light-induced decomposition of refrigerants/propellants like freons = chlorofluorocarbons = CFCs).

ClO can decompose on its own: $2ClO(g) \rightarrow Cl_2(g) + O_2(g)$

…consumes more ozone…

If $\frac{\Delta[ClO]}{\Delta t} = -2.95\times10^6\ Ms^{-1}$, what are the changes in $[Cl_2]$ & $[O_2]$?

ClO itself also reacts with ozone: $ClO(g) + O_3(g) \rightarrow O_2(g) + ClO_2(g)$

If $\frac{\Delta[ClO]}{\Delta t} = -9.03\times10^3\ Ms^{-1}$, what is the rate of disappearance of O_3 ?

NOTE: these are instantaneous rates…& usually NOT constant over time!
THUS: To predict how long it takes for "all the ozone to disappear", we must learn more about reaction kinetics!

Think small: In order for a reaction to occur…

The reacting molecules must:

- collide with one another
- with sufficient energy
- in an orientation that can lead to rearrangement of atoms

RATE DEPENDS ON:

- CONCENTRATION
- TEMPERATURE
- RXN'S STERIC REQUIREMENTS

Reaction conditions = factors that affect rate:

1) Concentration of reactants (15.3)
2) Temperature (15.5)
3) Presence of catalysts (15.5)

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Factors that affect rxn rates (15.2)

1.) concentration of reactants
- concentration (solutions)
- surface area (solids)
- pressure (gases)

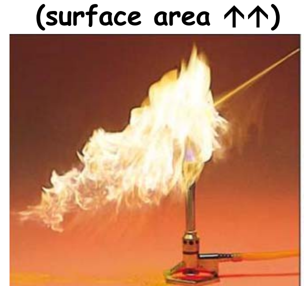
related to need for reactants to collide!

K&T Fig.15.6:
How quickly will some flammable spores burn?

DEPENDS ON SURFACE AREA

A pile of them doesn't burn well…

…a spray of powder burns RAPIDLY (surface area ↑↑)



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15.3 Effect of concentration on reaction rate

HIGHER CONCENTRATION OF REACTANTS

⇩

HIGHER RATE OF REACTION

but not always a *linear* relationship

- Molecules must COLLIDE! (more details on this later)
  If have more reactants in a given volume
  ⇒ more collisions between reactants…
  ⇒ faster reaction…

For a reaction: **reactant ⟶ product**

Rate = k [reactant]^n where k = "rate constant"
n = "order"

called a "rate law" & must be determined <u>by experiment</u>…

If a rxn uses a catalyst: catalyst written above the reaction arrow
& [catalyst] might appear in rate law too

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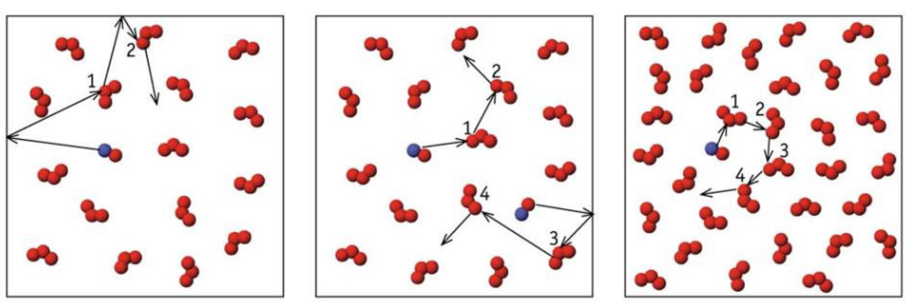
Concentration determines collision frequency



(a) 1 NO: 16 O_3 – 2 hits/second **(b)** 2 NO: 16 O_3 – 4 hits/second **(c)** 1 NO: 32 O_3 – 4 hits/second

THUS: can *<u>begin</u>* to read into information yielded by rate law

1st order *wrt* reactant "A" *<u>suggests</u>* collision involving 1 molecule of A
2nd order *wrt* reactant "A" *<u>suggests</u>* collision involving 2 molecules of A

→ only will give us a feeling about the rxn's slowest step…
we'll see more about this soon…

K&T Fig.15.11

(20)

Rate laws describe concentration dependence

- For rxns that occur in EXACTLY one collision:
  - → each reactant molecule is important
  - → conc. dependence easy to predict
  - → can use stoichiometry to find rate law

IMPORTANT: THIS IS NOT GENERAL !
ONLY FOR **1-COLLISION** REACTIONS !

REMEMBER: the realm of kinetics = RXN PATHWAYS

Reaction "mechanism" = sequence of collisions or steps that add up to yield overall rxn

If we do NOT know the exact mechanism of the rxn, we CANNOT predict the reaction's rate law.

THUS: RATE LAWS ARE ALWAYS FIRST DETERMINED BY EXPERIMENT !

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↳ next…

ASSIGNED READINGS:

BEFORE NEXT CLASS:

Read: Ch.15 up to section 15.2

+ WORK ON Problems from Ch.14-15

Next class: Ch.15…