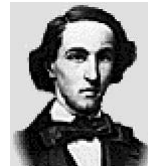**ASSIGNED READINGS:**

TODAY'S CLASS: Ch. 19.5-19.6
                    brief solutions review

Remember: Chem 101 seminars this week

(1)

Chemists usually summarize net driving force in ENERGY terms (rather than entropy)…

J. Willard Gibbs
1839-1903

To derive: start with 2nd law, in system's perspective:

$$\Delta S^o_{univ} = \Delta S^o_{sys} - \frac{\Delta H^o_{sys}}{T} \ .... \quad \text{If} > 0 \Rightarrow spontaneous$$

(note:
 no subscript
 $\Rightarrow$ system.)

Convert to E terms: Multiply by –T & put enthalpy 1st

$$-T\Delta S^o_{univ} = \Delta H^o_{sys} - T\Delta S^o_{sys} \equiv \Delta G^o = \Delta H^o - T\Delta S^o$$

= <u>net</u> E dissipated as
   disorder in the universe…

"Gibbs Free Energy" *(state function)*

LARGER –ve # = GREATER DRIVING FORCE

If ΔS^o_{univ} is…	Then ΔG^o is…	Rxn described as…	Driven to proceed…
positive	negative	spontaneous	forwards
negative	positive	non-spontaneous	backwards
zero	zero	at equilibrium	none

2nd law rephrased again: Spontaneous processes have $\Delta G < 0$.
A process will be spontaneous in the direction that <u>releases free energy</u>.
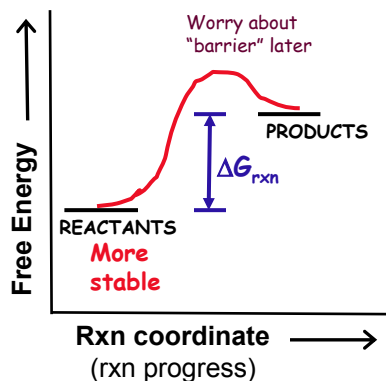
Picturing relative free energies: ENERGY DIAGRAMS
(also called "reaction coordinate" or "reaction progress" diagrams)

"Exergonic" process: $\Delta G < 0$
overall have energy released
when rxn proceeds forward
"DOWNHILL IN ENERGY"

Worry about this "barrier" later...kinetics!

REACTANTS

ΔG_{rxn}

More stable

PRODUCTS

Free Energy

Rxn coordinate ⟶
(rxn progress)
almost like a time axis
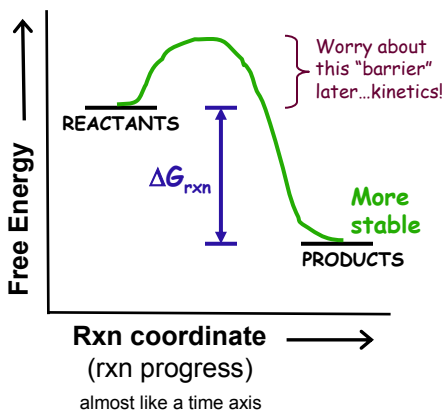
(3)

"Endergonic" process: $\Delta G > 0$
overall must input energy
for rxn to proceed forward
"UPHILL IN ENERGY"

Worry about "barrier" later

PRODUCTS

ΔG_{rxn}

REACTANTS
More stable

Free Energy

Rxn coordinate ⟶
(rxn progress)

EXAMPLE: Why is graphite more stable than diamond?
i.e., why is $\Delta G_{d \to gr} < 0$?

DIAMOND →
• network solid
• each C has:
   4 C-C bonds
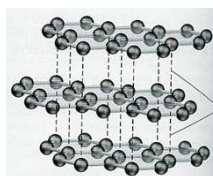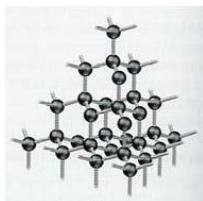
← GRAPHITE
• layered solid
• each C has:
   2 C-C bonds
   1 C=C bond
   weak interactions
      with adjacent
      layers

(4)

The reaction: $2\ Mg(s) + O_2(g) \rightarrow 2\ MgO(s)$ is highly spontaneous at room temperature and has a negative value for $\Delta S°$. The second law of thermodynamics states that in any spontaneous process, there is always an increase in the entropy of the universe. Is there an inconsistency between the above reaction and the second law? <u>Explain.</u>
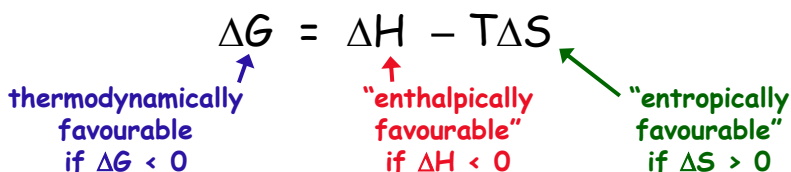
General approach: clearly identify question being asked
                              & comment on each aspect of problem

Thus:

1. Question = is this rxn violating the 2nd law?
2. Identify criteria for spontaneity
3. Comment on fact that rxn has $\Delta S° < 0$ (*i.e.,* say why)
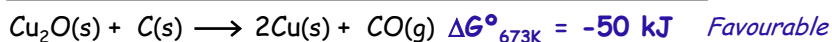4. Specifically relate this to the 2nd law
5. Conclude: violation or not?

(5)

How much free energy (driving force) ?
  ...balance between system's change in enthalpy & entropy

$$\Delta G\ =\ \Delta H\ -\ T\Delta S$$

thermodynamically   **"enthalpically**   **"entropically**
favourable   **favourable"**   **favourable"**
if $\Delta G < 0$ **if $\Delta H < 0$**   **if $\Delta S > 0$**

ΔG = net evolution of energy by system   ("-" means E released)
- difference between heat evolved & the organizational energy
  = maximum energy available or "FREE" for doing useful work
     such as driving less favourable processes forward...

**Goal: extract copper from a common copper ore, copper (I) oxide:**

$Cu_2O(s) \longrightarrow 2Cu(s) + \frac{1}{2}O_2(g)$ $\Delta G°_{673K}$ = **+125 kJ**   *Won't go...*

$C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g)$ $\Delta G°_{673K}$ = **–175 kJ**   *But, if add charcoal...*

$Cu_2O(s) + C(s) \longrightarrow 2Cu(s) + CO(g)$ $\Delta G°_{673K}$ = **–50 kJ**   *Favourable*

  "coupled reactions"   *Bronze Age metallurgists' method*

Coupled reactions: *very important in biology!*

Most biological reactions occur by harnessing energy "stored in ATP"
- hydrolysis of bond between ADP and phosphate releases energy
   (important: not ONLY breaking a bond here, which requires E...making new ones too!)
- this energy used to drive endergonic reactions occurring nearby
       e.g., building new molecules of protein, etc.

$$ATP^{4-} + H_2O$$

$$ADP^{3-} + HPO_4^{2-} + H^+$$
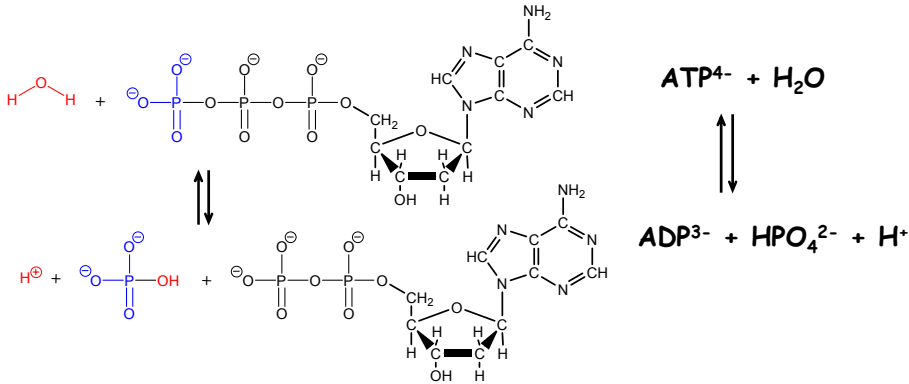
Under physiological conditions: $\Delta G^{o'} = -30.5$ kJ $\Rightarrow$ $K = 12.3$ (product favoured)
- favoured by entropy (creating more particles)
- favoured by enthalpy (new P-O bond <u>much</u> more stable than original P-O bond,
  due to less repulsion of adjacent $\ominus$ charges...makes up for breaking OH)

Free energy & chemical reactions

$\Delta G^o{}_{rxn}$(reactants in std states → 100% products in std states) **via 2 approaches:**

1) **DIRECT**: Hess's law with $\Delta G^o{}_f$ s (from thermodynamic data tables)

   - $\Delta G^{\circ}{}_f$ = free energy of formation of ____ from std state elements
   - $\Delta G^o{}_f$ = 0 for std state elements themselves
      · by def'n, like for ΔH $\Rightarrow$ don't calculate using $\Delta G = \Delta H - T\Delta S$

2) **INDIRECT**: if $\Delta G^o{}_f$ values unavailable
   - Calculate $\Delta H^o{}_{rxn}$ and $\Delta S^o{}_{rxn}$ using Hess's law
   - Use $\Delta G_{rxn} = \Delta H^o{}_{rxn} - T\Delta S^o{}_{rxn}$
   - Very useful $\Rightarrow$ lets us consider T ≠ 298 K
                 ...also, can predict what T is needed!

BE AWARE: $\Delta G = \Delta H - T\Delta S$ is only truly accurate at T = 298K
· if we calculate $\Delta G^o{}_{rxn}$ at T ≠ 298 K, we are assuming
  that enthalpy & entropy changes are same at all temperatures
· NOT absolutely true... but only a problem if we try to compare
  data calculated for VERY different temperatures (>>1000K apart)

Elemental sulfur forms at volcano vents

This reaction is believed to be involved:

$$SO_2(g) + 2 H_2S(g) \rightarrow 3 S(s) + 2 H_2O(g)$$
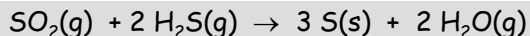
1. Is the formation of elemental sulfur via this reaction thermodynamically favourable at RT (298 K)?
2. If the gas mixture is the same in both locations, would there be more S(s)...
   a) ...in the volcano's interior?
   b) ...at the mouth of the vent?   *WHY?*

SO_2, H_2S, CO_2, *etc*
S(s)
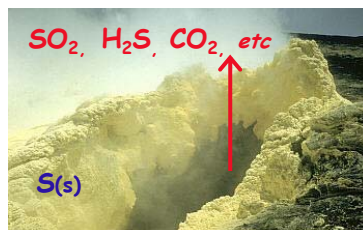
Substance (298 K)	ΔH^o_f (kJ/mol)	S^o_f (J/mol·K)
$SO_2(g)$	-296.8	248.2
$H_2S(g)$	-20.17	205.6
S(s)	0	32.1
$H_2O(g)$	-241.8	188.7

ANS:
$\Delta H^o = -146.5$ kJ
$\Delta S^o = -185.7$ J/K
$\Delta G^o = -91.1$ kJ... so...?

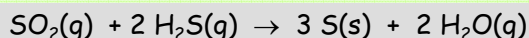**Images:** http://volcanoes.usgs.gov/Products/Pglossary/fumarole.html
http://vulcan.wr.usgs.gov/Imgs/Jpg/MSH/Images/MSH82_st_helens_plume_from_harrys_ridge_05-19-82_med.jpg

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How low does the temperature <u>need</u> to be for this entropically unfavourable reaction to be product-favoured?

$$SO_2(g) + 2 H_2S(g) \rightarrow 3 S(s) + 2 H_2O(g)$$

General approach to probe temperature dependence:

$\Delta G_{rxn} = \Delta H^o_{rxn} - T\Delta S^o_{rxn} < 0$ **for rxn to proceed fwd**

Let: $\Delta H^o_{rxn} - T\Delta S^o_{rxn} = 0$ ⇨ solve for temperature where
NO NET RXN WILL OCCUR...
= standard-state equilibrium
(balance of enthalpy & entropy terms)

So, for S(s)-deposition:

$\Delta H^o = -146.5$ kJ
$\Delta S^o = -185.7$ J/K

ANS: rxn spontaneous at low temperatures (T < 515 °C)
*& more product-favoured as temperature is **lowered***

Driving force depends on temperature: $\Delta G = \Delta H - T\Delta S$

ΔH^o_{sys}	ΔS^o_{sys}	Spontaneous ?	Process is…
Exothermic $\Delta H^o_{sys} < 0$	**Less order** $\Delta S^o_{sys} > 0$	Spontaneous under all conditions	**Enthalpically & entropically driven**
Exothermic $\Delta H^o_{sys} < 0$	More order $\Delta S^o_{sys} < 0$	Depends on relative magnitudes of ΔH & ΔS; **more favourable at low T**	**Enthalpically favourable** (driven by ΔH)
Endothermic $\Delta H^o_{sys} > 0$	**Less order** $\Delta S^o_{sys} > 0$	Depends on relative magnitudes of ΔH & ΔS; **more favourable at high T**	**Entropically favourable** (driven by ΔS)
Endothermic $\Delta H^o_{sys} > 0$	More order $\Delta S^o_{sys} < 0$	Not spontaneous under ANY conditions	Enthalpically & entropically unfavourable

Another temperature-dependence example

EX.: Removing iron from hematite ore

$$2Fe_2O_{3(s)} + 3C_{(s,graphite)} \rightarrow 4Fe_{(s)} + 3CO_{2(g)}$$

a) This process carried out in a blast furnace. Why?
b) What is the minimum T at which this rxn is spontaneous?
   (& confirm that it is spontaneous above this T but not below…)

Substance (298 K)	ΔH^o_f (kJ/mol)	S^o_f (J/mol·K)
$Fe_2O_{3(s)}$	-826	90
$C_{(s,gr)}$	0	6
$Fe_{(s)}$	0	27
$CO_{2(g)}$	-393.5	214

REMEMBER: hotter is NOT always better! Must consider ΔH *vs.* ΔS

(12)

$$2Fe_2O_3(s) + 3C(s,graphite) \rightarrow 4Fe(s) + 3CO_2(g)$$

ΔH°_{rxn} = [4(0)+3(-393.5)]-[2(-826)+3(0)] = 471.5 kJ *per 2 mol Fe$_2$O$_3$*
enthalpically unfavourable

ΔS°_{rxn} = [4(27)+3(214)]-[2(90)+3(6)] = 552 J/K   *per 2 mol…*
= 0.552 kJ/mol·K   UNITS!
entropically favourable

Let $\Delta H^\circ_{rxn} - T\Delta S^\circ_{rxn}$ = 0
⇨ T = $(\Delta H^\circ_{rxn})/(\Delta S^\circ_{rxn})$ = (471.5 kJ/mol) / (0.552 kJ/mol·K)
⇨ T = 854 K
⇨ T = 581 °C *at this temp, no net rxn…*

Test if rxn should occur at T > 854 K (let's try 900 K):
$\Delta G^\circ_{rxn} = \Delta H^\circ_{rxn} - T\Delta S^\circ_{rxn}$
= (471.5 kJ/mol) – (900 K)(0.552 kJ/mol·K)
= -25.3 kJ/mol   NEGATIVE !   Spontaneous!
⇨ **rxn spontaneous at high temperatures (T > 581 °C)**
= more product-favoured as we raise temperature

(13)

Thermodynamics (enthalpy, entropy, free energy) provides
us with a foundation for building an understanding of why
things happen...

CHAPTERS 13-14: Properties of Solutions

FOCUS ON LIQUID-PHASE SOLUTIONS:
Solvent = a liquid
Solute = some other compound

Physical properties of solvent are influenced
(in a predictable way) by dissolved solutes. *WHY?*

OUR APPROACH:
1.) remember what dissolution means (REVIEW Ch.5!)
2.) learn why liquids behave the way they do -- Ch.13
3.) learn how solutes affect this   -- Ch.14

(14)

ONE ionic bond has similar strength to ONE covalent bond

• ions have ≥ 1 unit of "+" or "–" charge on them
• note: **ionic bonds** involve ions packing close together
        with **no direction requirement**…so they can be **easily rearranged**
                                              & replaced with others
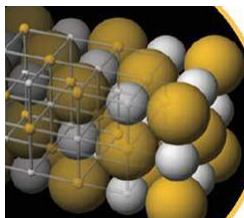
*An ionic crystal consists
of many many individual
ionic bonds.*

vs.: **covalent bonds** involve sharing of electron pairs,
        ⇨ atoms locked together in **fixed orientations**
        ⇨ rearranging these bonds is difficult
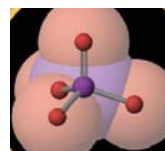
*BUT: A molecular crystal is held together by
       relatively weak NON-covalent intermolecular forces…*

(15)

Dissolution: particles change nearest neighbours

Molecular compounds:
■ intact molecules disperse
■ covalent bonds DO NOT break
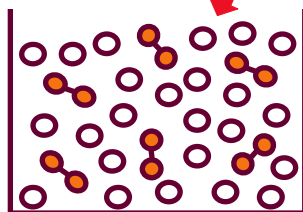
Ionic compounds:
■ bonds between ions break
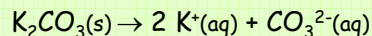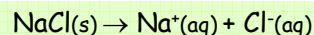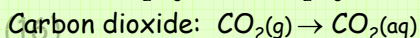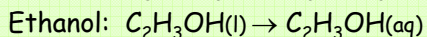■ polyatomic ions remain intact

**Molecules
surrounded
by own kind**
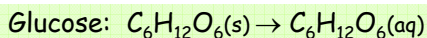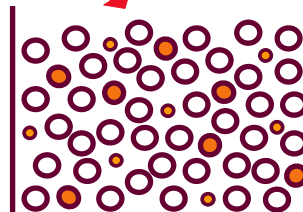
IN PURE
SUBSTANCE…

**Cations
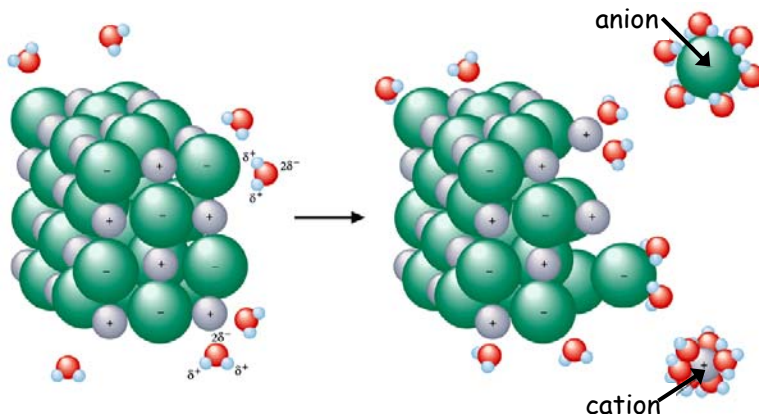in contact
with anions**

IN SOLUTION:
each molecule/ion
surrounded by
solvent molecules

Glucose: $C_6H_{12}O_6(s) \rightarrow C_6H_{12}O_6(aq)$
Ethanol: $C_2H_3OH(l) \rightarrow C_2H_3OH(aq)$
Carbon dioxide: $CO_2(g) \rightarrow CO_2(aq)$

$NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$
$K_2CO_3(s) \rightarrow 2\ K^+(aq) + CO_3{}^{2-}(aq)$

(16)

Dissolving a SALT

Water molecules surround or "hydrate" the ions!

anion

cation

Energetics of system:

Enthalpic view: ionic bonds → ion–to–H_2O interactions
Entropic view: crystal + random H_2Os → solvated ions + organized H_2Os
OVERALL: actually quite difficult to predict ΔH and ΔS here…

(17)

What factors affect solubility?

Why are some substances soluble in water but not in paint thinner?

"LIKE DISSOLVES LIKE" BUT…WHY??!!

OTHER QUESTIONS:

Why do some substances require heat to dissolve and others do not?

What determines the quantity of substance that dissolves?

Why will some substances not stay mixed?

INTERMOLECULAR FORCES MUST BE CONSIDERED…

BEFORE WE DO THIS: REVIEW Ch.9 on your own!
must re-**master** Lewis structures, geometries & polarities

BEFORE NEXT CLASS:

Read: Ch.19 up to 19.6, 19.8 (read 19.7 after Ch.16)

   + WORK ON Problems from Ch.19

   (Qs that don't refer to "K" or equilibrium)

Next class: Ch.13.1-13.5…

(19)