"A" students work (without solutions manual) ~ 10 problems/night.
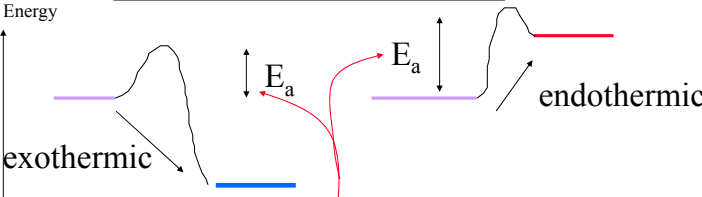
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Module #20
Spontaneity

Effect of number of Possible configurations (randomness) on reactions

---

What we've Learned So Far

Energy
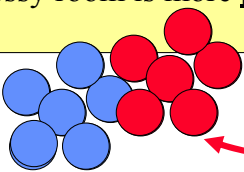
E_a

E_a

endothermic

exothermic

$A + B \longrightarrow C + heat$

$A + B + heat \longrightarrow C$

$rate = k[A][B]$

$rate = \left(A \exp^{-\frac{E_a}{RT}} \right)[A][B]$

Does **not** tell us if **spontaneous** or not
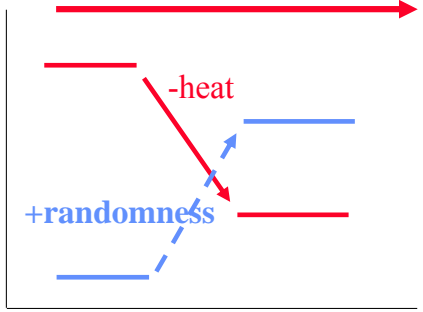

A messy room is more **probable** than an organized one.

Can think of this as **stored** energy.

spontaneous? or probable?

Spontaneous Reactions:

heat

or
randomness

-heat

+randomness

reactants   products

-heat
+ randomness

-ΔH
+S

OJO

1

Randomness = more possibilities = **entropy** (S)

What is the most probable configuration for **n** tossed quarters?

2 coins

1 coin =2 sides

2

1

2 configurations =2^1

4 configurations =2^2

1

Most probable configuration is least organized
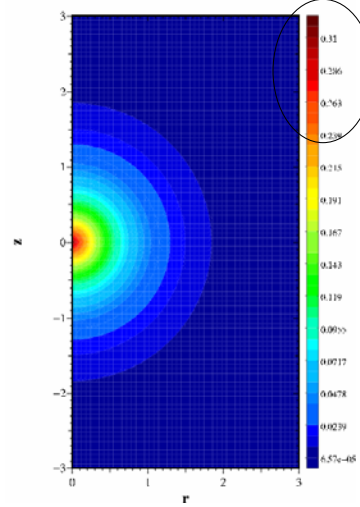
What will the pattern be for three coins?

1   3   3   1

3 coins
8 configurations = 2^3
4 coins
? configurations = $2^?$

#$configurations = 2^n$

1. Most probable configuration is least organized
2. Number of possible configuration increases exponentially
3. No. configurations contains information about compound (sides)

Probability of finding
An electron – everywhere!
Very random

How does this affect the trends in entropy of various elements?

1s electron

2p electron probability
Is more confined – less
Random, less entropy

2

Probability of
Finding an electron
For a d orbital –
More spatially constrained,
Less entropy

Entropy and Atomic Mass

Entropy of Pure Elements

1. Entropy contraction across row – related to organization of electrons
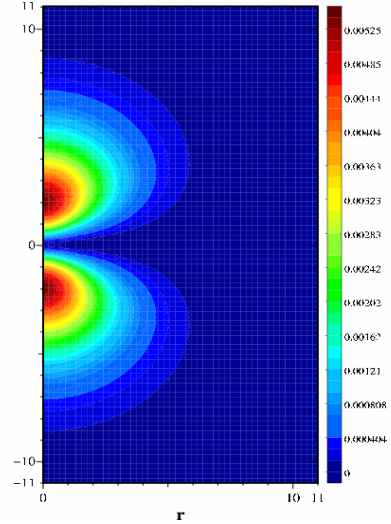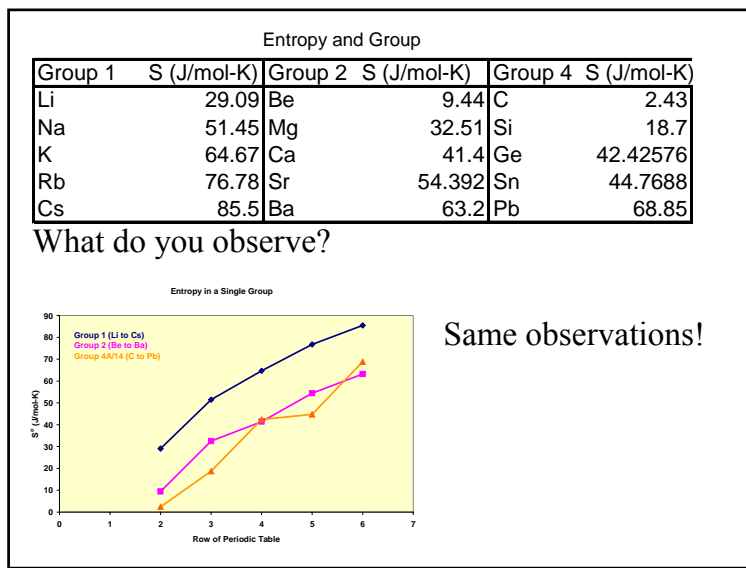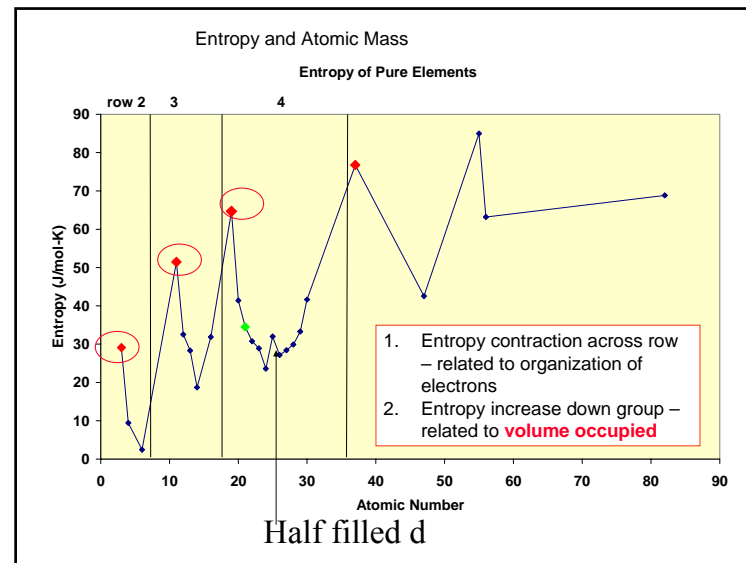2. Entropy increase down group – related to **volume occupied**

Half filled d

Entropy and Group

Group 1	S (J/mol-K)	Group 2	S (J/mol-K)	Group 4	S (J/mol-K)
Li	29.09	Be	9.44	C	2.43
Na	51.45	Mg	32.51	Si	18.7
K	64.67	Ca	41.4	Ge	42.42576
Rb	76.78	Sr	54.392	Sn	44.7688
Cs	85.5	Ba	63.2	Pb	68.85

What do you observe?

Entropy in a Single Group

Group 1 (Li to Cs)
Group 2 (Be to Ba)
Group 4/14 (C to Pb)

Same observations!

"A" students work
(without solutions manual)
~ 10 problems/night.

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**Module #20
Spontaneity**

Reaction Entropy

I WANT YOU
TO PRACTICE
EVERY DAY!

3

The change in entropy in a reaction is the difference between the summed entropy of the products minus the summed entropy of the reactants scaled by the number of moles

$$\Delta S_{rx} = \sum_{products} n_i S_i - \sum_{reac\tan ts} n_i S_i$$

---

1. $Cs_s \underset{\leftarrow}{\rightarrow} Cs_\ell$

2. $Cs_\ell \underset{\leftarrow}{\rightarrow} Cs_g$

	S° (J/mol-K)
$Cs_{(s)}$	85.15
$Cs_{(l)}$	92.07
$Cs_{(g)}$	175.6

$$\Delta S_{rx} = \sum_{products} n_i S_i - \sum_{reac\tan ts} n_i S_i$$

$$\Delta S_{rx} = \left(1mole_{Cs_\ell}\right)\left(92.07\frac{J}{mol_{Cs_\ell} \cdot K}\right) - \left(1mole_{Css}\right)\left(85.15\frac{J}{mol_{Cs_s} \cdot K}\right)$$

$$\Delta S_{rx} = \left[\left(92.07\frac{J}{K}\right) - \left(85.15\frac{J}{K}\right)\right] = \left(6.92\frac{J}{K}\right)$$

Example Calculation 1: Calculate the change in reaction entropy that occurs for each of the following two phase changes given the data below:
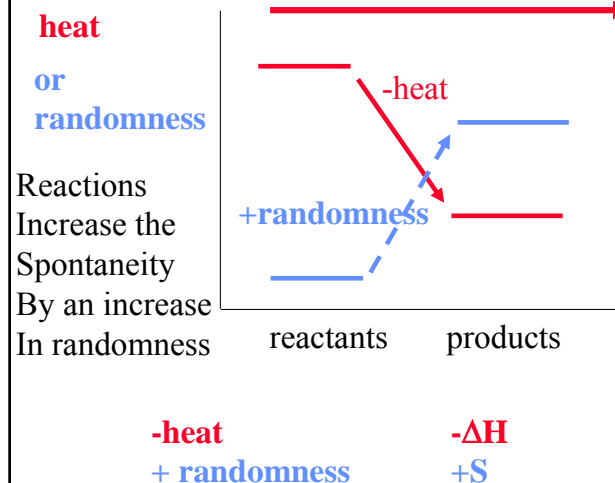
1. $Cs_s \underset{\leftarrow}{\rightarrow} Cs_\ell$

2. $Cs_\ell \underset{\leftarrow}{\rightarrow} Cs_g$

	S° (J/mol-K)
$Cs_{(s)}$	85.15
$Cs_{(l)}$	92.07
$Cs_{(g)}$	175.6

$$\Delta S_{rx} = \sum_{products} n_i S_i - \sum_{reac\tan ts} n_i S_i$$

$$\Delta S_{rx} = \left(1mole_{Cs_g}\right)\left(175.6\frac{J}{mol_{Cs_g} \cdot K}\right) - \left(1mole_{Cs\ell}\right)\left(92.07\frac{J}{mol_{Cs_\ell} \cdot K}\right)$$

$$\Delta S_{rx} = \left[\left(175.6\frac{J}{K}\right) - \left(92.07\frac{J}{K}\right)\right] = \left(83.53\frac{J}{K}\right)$$

Spontaneous Reactions:

heat

or randomness

Reactions Increase the Spontaneity By an increase In randomness

-heat

+randomness

reactants   products

-heat   -ΔH
+ randomness   +S

4

Slide 1

	S° (J/mol-K)
$H_2O_{(l)}$	69.91
$H_2O_{(g)}$	188.83
$Hg_{(l)}$	77.40
$Hg_{(g)}$	174.89
$Cs_{(s)}$	85.15
$Cs_{(l)}$	92.07
$Cs_{(g)}$	175.6

"Medicine is the Art of Observation" (Al B. Benson)

What do you observe?

Entropy Changes of Cs With Phase

(y-axis: S° (J/mol-K), 0 to 200; x-axis: solid, liquid, gas)

1. Large change liquid to gas
2. S depends on Temp!!!

Slide 2

Possible configurations?

solid < glass, plastic, liquid < gas

$$S_{solid} < S_{solid, plastic, liquid} < S_{gas}$$

S

Absolute Zero, no motion

T (K)

Note: this Refers to a single Molecule or element Water ice, liquid, gas

Slide 3

A closely related idea to change in entropy
In phase changes is the change in entropy in
Going from individual ligands to chelates

From **Module 18** we considered the electrostatic attraction between the electron pairs on ligand functional groups and the positive nucleus of a metal ion.

Module 18 review

Slide 4

$$E_{el} = k\left(\frac{q_1 q_2}{r_1 + r_2}\right)$$

$\left[Cu(NH_3)_4\right]^{2+}$

z
x
y

x^2-y^2

Module 18 review

5

Panel 1 (top-left)

$$K_{rx} = K_{f1}K_{f2}K_{f3}K_{f4}K_{f5}K_{f6}\ldots\ldots K_{fn}$$

We observed that multidentate ligands had very high K_f values

Lead Complexation Constants

Ligand	logK1	logK2	LogK3	logK4	logKf
F-	1.4	1.1			2.5
Cl-	1.55	0.6	-0.4	-0.7	1.05
Br-	1.8	0.8	-0.1	-0.3	2.2
I-	1.9	1.3	0.7	0.6	4.5
OH-	6.3	4.6	2		12.9
Acetate	2.7	1.4			4.1
Oxalate	4.9	1.9			6.8
Citrate	5.7				5.7
EDTA	17.9				17.9

Which are polydentate?
What do you observe?

Why so large?

Module 18 review

Panel 2 (top-right)

Note that the electrostatic attraction which shows up in the enthalpy is similar for both compounds

$$M\left(NH_2CH_3\right)_4\left(X\right)_2 + 2en \rightleftharpoons M(en)_2\left(X\right)_2 + 4NH_2CH_3$$

NH_2CH_3

Panel 3 (bottom-left)

Example 2: Predict the entropy change in the following reaction by considering volume occupied and number of possible configurations between the reactants and products

$$\underbrace{M\left(NH_2CH_3\right)_4\left(X\right)_2 + 2en}_{3} \rightleftharpoons \underbrace{M(en)_2\left(X\right)_2 + 4NH_2CH_3}_{5}$$

		ΔS^o_{exp}	ΔS^o_{calc}
$Cd\left(NH_3CH_3\right)_4^{2+} + 2en \rightarrow Cd(en)_2^{2+} + 4NH_3CH_3$		$79.5\dfrac{J}{mol\cdot K}$	$58.5\dfrac{J}{mol\cdot K}$

J. Chem. Ed. 61,12, 1984, Entropy Effects in Chelation Reactions, Chung-Sun Chung

Panel 4 (bottom-right)

Example Calculation 3: Calculate the reaction entropy changes for the reaction shown below given:

$$CuS_s + Cu_s \rightarrow Cu_2S_s$$

		S° (J/mol-K)
S	rhombic	32
S	orthoclinic	33
$Cu_{(s)}$		85.15
$CuS_{(s)}$		92.07
$Cu_2S_{(s)}$		175.6

First let's think about this a bit

1. Internal Entropy
   a. Why should CuS have more entropy than Cu?
   b. Why should Cu$_2$S have much more entropy than CuS?

Slide 1 (top left)

$$CuS_s + Cu_s \rightarrow Cu_2S_s$$

Which one might have
More configurations?

http://www.haraldthielenredlich.onlinehome.de/kkch/cu1+cu2s.jpg

http://images.google.com/imgres?imgurl=http://www.unisa.edu.au/synchrotron/res/projects/chalcociteCu2S.jpg&imgrefurl=http://www.unisa.edu.au/synchrotron/res/projects/default.asp&h=242&w=180&sz=20&hl=en&start=7&um=1&tbnid=UYBN7p1lBciHwM:&tbnh=110&tbnw=82&prev=/images%3Fq%3DCu2S%2B%26svnum%3D10%26um%3D1%26hl%3Den%26client%3Dfirefox-a%26channel%3Ds%26rls%3Dorg.mozilla:en-US:official%26sa%3DG

Slide 2 (top right)

A single, individual, H atom can occupy 4
Different locations – thus the compound will be

	S^o (J/mol-K)
CH_4	186.
C_2H_4	219.4

More random than one with three locations for
The hydrogen

This reflects **internal entropy** which often scales
with # of Atoms in the molecule.

Slide 3 (bottom left)

Entropy and Molecular Structure:

$$(\#configurations) = z^n$$

	S, J/mol-K
$O^{(g)}$	161
$O_{2(g)}$	205
$O_{3(g)}$	237.6
$C_{(g)}$	158.O
$CO_{(g)}$	197.9
$CO_{2(g)}$	213.6
$Cl_{(g)}$	165.2
$Cl_{2(g)}$	2232.96
Pb	68.85
PbO	68.70
PbO_2	76.98
Pb_3O_4	209.2
CH_4	186.4
C_2H_4	219.4
C_2H_2	200.8
C_2H_4	219.4
C_2H_6	229.5

Have we
Convinced
Ourselves
Yet?

| Species type	Orientation of electron pairs	Predicted bond angles	Example	Ball and stick model
AX_2	Linear			
AX_3	Triangular planar		"z" = 2	
AX_4	Tetrahedron		"z" = 4	
AX_5	Triangular bipyramid		"z" =6	
AX_6	Octahedron		"z" = 8	

Slide 4 (bottom right)

Internal Entropy and Molecular Structure:

$$(\#configurations) = z^n$$

Internal Entropy is generally increasing
With number of atoms in the molecule
Because the number of locations within the molecule
Where an atom could be found is increasing and
Because the possible orientations of the molecule increases

1, average=38.26
2, average=62.15
3, average = 95.42
4, average=137.9
5, average 103
6, average- 124

Reliability of average
decreases with number
of averaged data points

Number observed

Entropy (J/mol-K)

Example Calculation 3: Calculate the reaction entropy changes for the reaction shown below given:

		S° (J/mol-K)
S	rhombic	32
S	orthoclinic	33
$Cu_{(s)}$		85.15
$CuS_{(s)}$		92.07
$Cu_2S_{(s)}$		175.6

$$CuS_s + Cu_s \rightarrow \underbrace{Cu_2S_s}$$
$$\underbrace{}_{2} \quad \underbrace{}_{1}$$
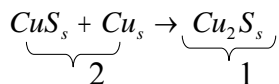
First let's think about this a bit

2. Spatial Volume of rx entropy

Which will be more imp in rx entropy? Internal entropy or spatial volume entropy?

We take two separate chemical units and make Them into 1 chemical unit – implies decrease in entropy

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Example Calculation 3: Calculate the reaction entropy changes for the reaction shown below given:

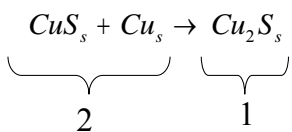|		S° (J/mol-K)
S	rhombic	32
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$Cu_{(s)}$		85.15
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$$CuS_s + Cu_s \rightarrow Cu_2S_s$$
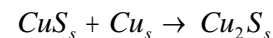
$$\Delta S_{rx} = \sum_{products} n_i S_i - \sum_{reac\,tan\,ts} n_i S_i$$

$$\Delta S_{rx} = \left(1mole_{Cu_2S_s}\right)\left(175.6\frac{J}{mol_{Cu_2S_s}\cdot K}\right)$$
$$- \left[\left(1mole_{Cu_s}\right)\left(85.15\frac{J}{mol_{Cu_s}\cdot K}\right) + \left(1mole_{CuS_s}\right)\left(92.07\frac{J}{mol_{CuS_s}\cdot K}\right)\right]$$

$$\Delta S_{rx} = \left(175.6\frac{J}{K}\right) - \left[\left(85.15\frac{J}{K}\right) + \left(92.07\frac{J}{K}\right)\right]$$

Example Calculation 3: Calculate the reaction entropy changes for the reaction shown below given:

		S° (J/mol-K)
S	rhombic	32
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$$CuS_s + Cu_s \rightarrow Cu_2S_s$$
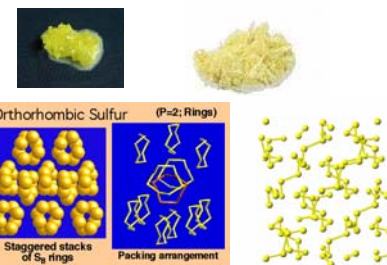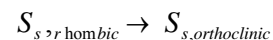$$\underbrace{}_{2} \quad \underbrace{}_{1}$$

$$\Delta S_{rx} = \left(175.6\frac{J}{K}\right) - \left[\left(85.15\frac{J}{K}\right) + \left(92.07\frac{J}{K}\right)\right]$$
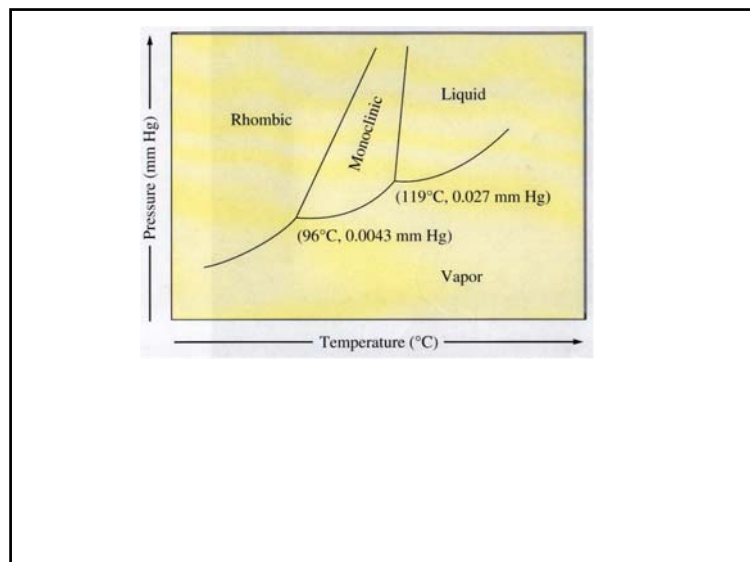$$\Delta S_{rx} = \left(175.6\frac{J}{K}\right) - \left[\left(177.22\frac{J}{K}\right)\right] = \left(-1.62\frac{J}{K}\right)$$

Example Calculation 4: Calculate the change in entropy for the allotropic forms of elemental S

		S° (J/mol-K)
S	rhombic	32
S	orthoclinic	33
$Cu_{(s)}$		85.15
$CuS_{(s)}$		92.07
$Cu_2S_{(s)}$		175.6

$$S_{s,r\,hom\,bic} \rightarrow S_{s,orthoclinic}$$

Gr: *allos* = others

Phase diagram: Pressure (mm Hg) vs Temperature (°C). Regions labeled Rhombic, Monoclinic, Liquid, Vapor. Points: (119°C, 0.027 mm Hg) and (96°C, 0.0043 mm Hg).

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Module #20
Spontaneity

Entropy of the surroundings

Spontaneous Process: Universal entropy increases

(The universe is winding down.)

$$\Delta S_{total\,(universe)} = \Delta S_{system\,(chemical\,rx)} + \Delta S_{surroundings}$$

$$\Delta S_{universe} > 0 \equiv spon\tan eous$$

Example 1: $S_{surroundings}$

$$C_s + O_{2,g} \rightarrow CO_{2,g} + heat$$

Change in $S_{surroundings}$?
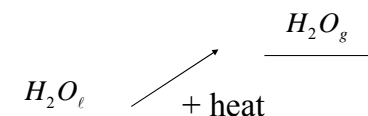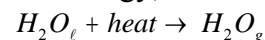
Change in $S_{reaction}$?

More organized (fewer molecules)
implies less entropy, less random
$\Delta S_{reaction} < 0$

heat will
increase
kinetic
energy of
gases =
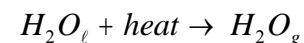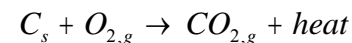$\Delta S_{surround} > 0$

9

Example 2: S$_{surroundings}$

From surroundings, withdraw heat,
Less kinetic energy, less motion, less entropy

$$H_2O_\ell + heat \rightarrow H_2O_g$$

H_2O_g

H_2O_ℓ + heat

Although this process requires
heat, it is **spontaneous**, driven
by **entropy of chemical reaction**

Reaction less random $\longrightarrow$ rx more random

The two reactions (the system)

$$C_s + O_{2,g} \rightarrow CO_{2,g} + heat$$

$$H_2O_\ell + heat \rightarrow H_2O_g$$

Interact with the surroundings by exchange of heat

Heat of reaction must be related to entropy of
surroundings

"A" students work
(without solutions manual)
~ 10 problems/night.

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Module #20
Spontaneity

Randomness of the
"surroundings" affected
By enthalpy

$$\Delta S_{total\,(universe)} = \Delta S_{system\,(chemical\,rx)} + \Delta S_{surroundings}$$

related to **enthalpy**
or heat of reaction

$$\Delta S_{surroundings} \propto \Delta H_{reaction}$$

proportional

Where will impact on S$_{surroundings}$ be greatest?
  a.   1 J at 600°C
  b.   1 J at 25°C

10

Predict entropy change is largest at low temperatures

$$\Delta S_{surroundings} \uparrow as\ T \downarrow$$

$$\Delta S_{surroundings} \propto \frac{\Delta H_{reaction}}{T}$$

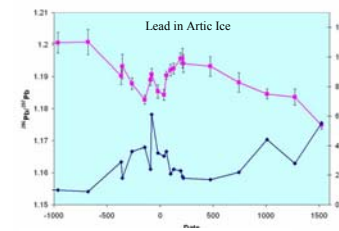$$\boxed{\Delta S_{surroundings} = -\frac{\Delta H_{reaction}}{T}}$$

sign change accounts for the fact that entropy increases with exothermic reactions

---

Historically Ag was mined as Ag_2S found in the presence of PbS, galena. Part of the process of releasing the silver required oxidizing the galena. The lead oxide recovered was used in glass making. The fumes often killed animals near by and have left a permanent record in the artic ice. Large regions near silver mines were deforested. One reason that this process was discovered so early in history was The low temperature at which it could be carried out.
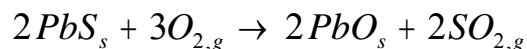

Lead in Artic Ice

Who has the "honor" of most contaminating The artic ice?   Medicine is the art of observation

Yorkshire, near old lead mines

Calculating S$_{surrounding}$ Example 1

$$2PbS_s + 3O_{2,g} \rightarrow 2PbO_s + 2SO_{2,g}$$

Compare the change in entropy of the surroundings for this reaction at room temperature and at the temperature of a campfire (~600 °C).
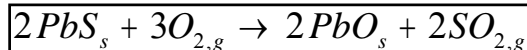
Know:	Don't know	red herrings?
reaction	entropy	none

$T = 25^o\ C$

$T = 600^o\ C$

$\Delta S_{surroundings} = -\frac{\Delta H_{reaction}}{T}$

$\Delta H^O = \sum n\Delta H^o_{f,products} - \sum n\Delta H^o_{f,reac\tan ts}$

$$2PbS_s + 3O_{2,g} \rightarrow 2PbO_s + 2SO_{2,g}$$

Substance	ΔH_f^0 (kJ/mole)
$O_{2(gas)}$	0
PbS	-100
PbO	-219
$SO_{2(gas)}$	-297

$\Delta H^O = \sum n\Delta H^o_{f,products} - \sum n\Delta H^o_{f,reac\tan ts}$

$\Delta H^O = \left\{ 2mole_{PbO_s}\left(\frac{-219kJ}{mole_{PbO_s}}\right) + 2mole_{SO_{2,s}}\left(\frac{-297kJ}{mole_{SO_{2,s}}}\right)\right\} - \left\{ 2mole_{PbS_s}\left(\frac{-100kJ}{mole_{PbS_s}}\right) + 3mole_{O_{2,s}}\left(\frac{0kJ}{mole_{O_{2,s}}}\right)\right\}$
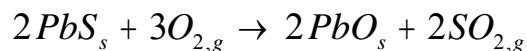
$\Delta H^O = \{-438kJ + -594kJ\} - \{-200kJ\}$

$\Delta H^O = -1032 + 200 = -832kJ$

$\Delta S_{surroundings} = -\frac{\Delta H_{reaction}}{T}$ $\Delta S_{surroundings} = -\frac{(-832kJ)}{T}$

11

Calculating S$_{surrounding}$ Example 1

$$2PbS_s + 3O_{2,g} \rightarrow 2PbO_s + 2SO_{2,g}$$

Compare the change in entropy of the surroundings for this reaction at room temperature and at the temperature of a campfire (~600 °C).

$$\Delta S_{surroundings} = -\frac{(-832kJ)}{T}$$

$T = 25^o\,C$

$T = 298K$

$T = 600^o\,C$

$T = 873K$

$$\Delta S_{surroundings} = -\frac{(-832kJ)}{298} = +2.792kJ$$

$$\Delta S_{surroundings} = -\frac{(-832kJ)}{873} = +0.953kJ$$

Our prediction was right! $\Delta S_{surroundings}$ Larger at low T

"A" students work (without solutions manual)
~ 10 problems/night.

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Module #20
Spontaneity

Total Entropy change
With reaction enthalpy

$$\Delta S_{total\,(universe)} = \Delta S_{system(chemical\,rx)} + \Delta S_{surroundings}$$

$$\Delta S_{surroundings} = -\frac{\Delta H_{reaction}}{T}$$

$$\Delta S_{total\,(universe)} = \Delta S_{system(chemical\,rx)} - \frac{\Delta H_{chemical\,rx}}{T}$$

Reaction Entropy Example Calculation 3 Compare the total entropy change for the following reaction at 25°C and 600°C

$$2PbS_s + 3O_{2,g} \rightarrow 2PbO_s + 2SO_{2,g}$$
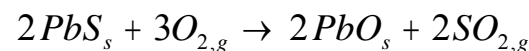
Substance	S^0 (J/K-mole)
O$_{2(gas)}$	205
PbS$_{(solid)}$	91
PbO$_{(solid)}$	66.5
SO$_{2(gas)}$	248

$$\Delta S_{rx} = \sum n_i S^o_{i,products} - \sum n_i S^o_{i,reac\tan ts}$$

$$\Delta S_{rx} = \left\{ 2mole_{PbO}\left(66.5\frac{J}{K \cdot mol_{PbO}}\right) + 2mole_{SO_2}\left(248\frac{J}{K \cdot mol_{SO_2}}\right)\right\}$$

$$-\left\{ 2mole_{PbS}\left(91\frac{J}{K \cdot mole_{PbS}}\right) + 3Mole_{O_2}\left(205\frac{J}{K \cdot mole_{O_2}}\right)\right\}$$

12

Reaction Entropy Example Calculation 3 Compare the total entropy change for the following reaction at 25°C and 600°C

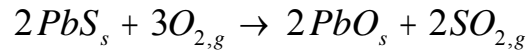$$2PbS_s + 3O_{2,g} \rightarrow 2PbO_s + 2SO_{2,g}$$

$$\Delta S_{rx} = \sum n_i S^o_{i,products} - \sum n_i S^o_{i,reac\,tan\,ts}$$

$$\Delta S_{rx} = \left\{ 2mole_{PbO}\left(66.5\frac{J}{K \cdot mol_{PbO}}\right) + 2mole_{SO_2}\left(248\frac{J}{K \cdot mol_{SO_2}}\right)\right\}$$
$$- \left\{ 2mole_{PbS}\left(91\frac{J}{K \cdot mole_{PbS}}\right) + 3Mole_{O_2}\left(205\frac{J}{K \cdot mole_{O_2}}\right)\right\}$$

$$\Delta S_{rx} = \left\{\left(143\frac{J}{K}\right)+\left(496\frac{J}{K}\right)\right\} - \left\{\left(182\frac{J}{K \cdot}\right)+\left(615\frac{J}{K \cdot}\right)\right\}$$

$$\Delta S_{rx} = -168\frac{J}{K}$$

$$\Delta S_{total\,(universe)} = \Delta S_{system(chemical\,rx)} - \frac{\Delta H_{chemical\,x}}{T}$$

$$\Delta S_{reaction} = -168\frac{J}{K} \qquad \Delta S_{surroundings} = -\frac{(-832kJ)}{T}$$

$$\Delta S_{total\,(universe)} = -168J - \frac{(-832kJ)}{T}$$

$T = 25^o\,C$	$T = 600^o\,C$
$\Delta S_{total\,(universe)} = -168\frac{J}{K} - \frac{(-832kJ)}{298K}$	$\Delta S_{total\,(universe)} = -168\frac{J}{K} - \frac{(-832kJ)}{873K}$
$\Delta S_{total)} = -168\frac{J}{K} + 2.791\frac{kJ}{K}$	$\Delta S_{total)} = -168\frac{J}{K} + 0.953\frac{kJ}{K}$
$\Delta S = -168\frac{J}{K} + 2,791\frac{J}{K}$	$\Delta S_{total} = -168\frac{J}{K} + 953\frac{J}{K}$
$\Delta S = 2623\frac{J}{K}$	$\Delta S_{total} = 785\frac{J}{K}$
Spontaneous	Less spontaneous

"A" students work (without solutions manual) ~ 10 problems/night.

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Module #20
Spontaneity

"Free energy" is a
Way of accounting
For contribution of randomness

I WANT YOU TO PRACTICE EVERY DAY!

$$\left(\Delta S_{total\,(universe)} = \Delta S_{system(chemical\,rx)} - \frac{\Delta H_{chemical\,r\,x}}{T}\right)T$$

$$-T\Delta S_{total\,(universe)} = -T\Delta S_{system(chemical\,rx)} + \Delta H_{chemical\,rx}$$

$$-T\Delta S_{total\,(universe)} = \Delta H_{chemical\,rx} - T\Delta S_{system(chemical\,rx)}$$

Define

$$-T\Delta S_{total\,(universe)} \equiv \Delta G_{free\,energy\,rx}$$

$$\Delta G_{free\,energy} = \Delta H_{r\,x} - T\Delta S_{rx}$$

Gibb's free energy
a) enthalpy of bonds
b) organization of atoms
c) randomness of surroundings

$$\Delta G_{free\,energy} < 0$$

Spontaneous reaction

13

Fitch Rule G3: Science is Referential

Conceptually:

$$\Delta G_{free\,energy} = \Delta H_{rx} - T\Delta S_{rx}$$

$$\Delta G_{free\,energy} < 0$$

ΔH reaction	ΔS reaction	Spontaneous?
-	+	always
+	+	at **high T**, 2nd term lg.
-	-	**at lowT**, 2nd term sm
+	-	never

Gibbs Free Energy Example 1

When will this reaction be spontaneous, hi or lo T?

$$2PbS_s + 3O_{2,g} \rightarrow 2PbO_s + 2SO_{2,g}$$

$$\Delta G_{free\,energy} = \Delta H_{rx} - T\Delta S_{rx}$$

$\Delta H_{rx}^O = \quad \Delta S_{rx}$
$-832kJ \quad = -168J$

ΔH reaction	ΔS reaction	Spontaneous?
-	+	always
+	+	at **high T**, 2nd term lg.
-	-	**at lowT**, 2nd term sm
+	-	never

At LowT!!!

Free Energy (kJ)

Non Spontaneous Reaction
Free Energy >0

More spontaneous

Spontaneous Reactions
Free Energy <0

Can we figure
Out exactly at what T
this reaction becomes
Spontaneous?

K

$$2PbS_s + 3O_{2,g} \rightarrow 2PbO_s + 2SO_{2,g} \qquad \Delta G_{free\,energy} = -832kJ\left(1 - T\left(-168\frac{J}{K}\right)\right)$$

14
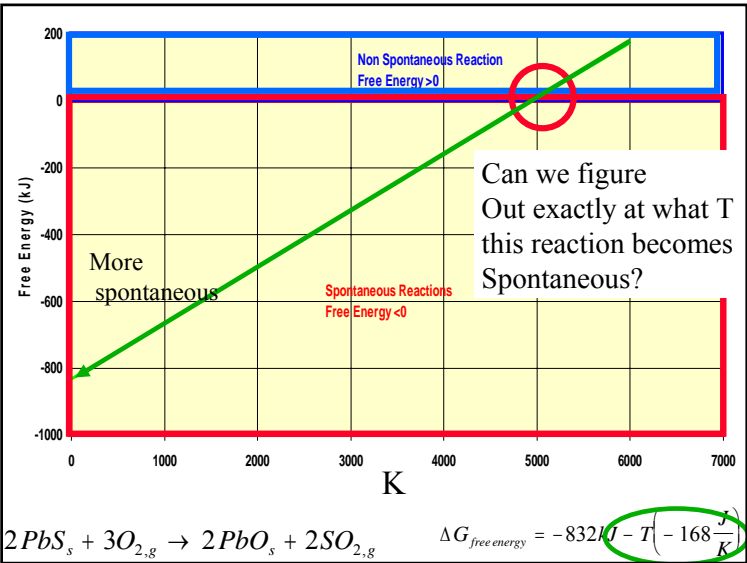
To find when a reaction will just go Spontaneous (or not)

1. Use the equation:
$$\Delta G_{free\,energy} = \Delta H_{rx} - T\Delta S_{rx}$$

2. Set ΔG^o to zero (equilibrium)
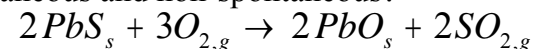$$0 = \Delta H_{rx} - T\Delta S_{rx}$$

3. Solve for T.
$$T\Delta S_{rx} = \Delta H_{rx}$$
$$T_{becomes\,spontaneous} = \frac{\Delta H_{rx}}{\Delta S_{rx}}$$

4. Depending upon sign of enthalpy entropy determine if temperature decrease/increase causes ΔG^o to go negative

---

Gibbs Free Energy Example 2

At what T will this reaction become change between Spontaneous and non-spontaneous?

$$2PbS_s + 3O_{2,g} \rightarrow 2PbO_s + 2SO_{2,g}$$

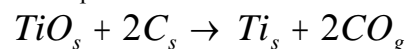$$\Delta G_{free\,energy} = \Delta H_{rx} - T\Delta S_{rx}$$

$$\Delta G_{free\,energy} = -832kJ - T\left(-168\frac{J}{K}\right)$$

$$0 = -832kJ - T\left(-168\frac{J}{K}\right)$$

$$832kJ = T\left(168\frac{J}{K}\right)$$

$$\frac{832kJ}{0.168\frac{kJ}{K}} = T$$

$$\boxed{4952K = T}$$

Rx spontaneous at T<4952K

Gibbs Free Energy Example 2: The only good substitute for $PbCO_3$ for white paint is TiO_2. To manufacture this paint need to be able to process titanium ore TiO_2. (Different allotrope). At what temperature does the following reaction become spontaneous?

$$TiO_s + 2C_s \rightarrow Ti_s + 2CO_g$$

Substance	ΔH_f^0 (kJ/mole)	S^0(J/K-mole)
Ti_{solid}	485	179.45
$CO_{(gas)}$	-110.5	198
$TiO_{2(solid)}$	-945	50
$O_{2(gas)}$	0	205
$SO_{2(gas)}$	-297	248
C_{solid}	0	0

$$\Delta G_{free\,energy} = \Delta H_{rx} - T\Delta S_{rx}$$

Substance	ΔH_f^0 (kJ/mole)	S^0(J/K-mole)
Ti_{solid}	485	179.45
$CO_{(gas)}$	-110.5	198
$TiO_{2(solid)}$	-945	50
$O_{2(gas)}$	0	205
$SO_{2(gas)}$	-297	248
C_{solid}	0	0

$$TiO_s + 2C_s \rightarrow Ti_s + 2CO_g$$

$$\Delta G_{free\,energy} = \boxed{\Delta H_{rx}} - \boxed{T\Delta S_{rx}}$$

$$\Delta G_{free\,energy} = \left\langle\left\{1mole\left(\frac{485kJ}{mole}\right) + 2mole\left(\frac{-110.5kJ}{mole}\right)\right\} - \left\{1mole\left(\frac{-945kJ}{mole}\right) + 2mole\left(\frac{0kJ}{mole}\right)\right\}\right\rangle$$

$$- T\left\langle\left\{1mole\left(\frac{179.45J}{K\cdot mole}\right) + 2mole\left(\frac{198J}{K\cdot mole}\right)\right\} - \left\{1mole\left(\frac{50J}{K\cdot mole}\right) + 2mole\left(\frac{0J}{K\cdot mole}\right)\right\}\right\rangle$$

$$\Delta G_{free\,energy} = \left\langle\{485 + 221\} - \{-945\}\right\rangle kJ$$

$$- T\left\langle\{575\} - \{50\}\right\rangle\frac{J}{K}$$

$$\Delta G_{free\,energy} = 1652kJ - T(525)\frac{J}{K}$$

Substance	ΔH_f^0 (kJ/mole)	S^0 (J/K-mole)
$TiO_{2\,solid}$	-945	50
Ti	485	179.45
$O_{2(gas)}$	0	205
$SO_{2(gas)}$	-297	248
C_{solid}	0	0
$CO_{(gas)}$	-110.5	198

$$TiO_s + 2C_s \rightarrow Ti_s + 2CO_g$$

$$\Delta G_{free\ energy} = \boxed{\Delta H_{rx}} - \boxed{T\Delta S_{rx}}$$

$$\Delta G_{free\ energy} = 1652kJ - T(525)\frac{J}{K}$$

When is this reaction spontaneous:
at high or low temp?

$$\boxed{T = 3144K}$$

$$0 = 1652 - T(0.525)$$

$$T(0.525) = 1652$$

Rx spontaneous > 3144K

Context Slide 1

titanium was not routinely processed until
after WWII (jet engine technology). So TiO_2 purified
not available cheaply for paint until after WWII

"A" students work
(without solutions manual)
~ 10 problems/night.

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Module #20
Spontaneity

Reference states for
Free Energy

As for enthalpy and entropy, there are tables
Of values obtained via Hess's Law

$$\Delta G^o_{,rx} = \sum n_i \Delta G^o_{f,i,products} - \sum n_i \Delta G^o_{fi,reac\tan ts}$$

f means formation at standard state 25 ºC!!!!!

16

Properties and Measurements		
Property	**Unit**	**Reference State**
Size	m	size of earth
Volume	cm^3	m
Weight	gram	mass of 1 cm^3 water at specified Temp (and Pressure)
Temperature	^{o}C, K	boiling, freezing of water (specified Pressure)
1.66053873x10^{-24}g	amu	(mass of 1C-12 atom)/12
quantity	mole	atomic mass of an element in grams
Pressure	atm, mm Hg	earth's atmosphere at sea level
Energy, General		
Animal	hp	horse on tread mill
heat	BTU	1 lb water 1 ^{o}F
	calorie	1 g water 1 ^{o}C
Kinetic	J	m, kg, s
Electrostatic		1 electrical charge against 1 V
electronic states in atom		Energy of electron in vacuum
Electronegativity F		

As for enthalpy and entropy, there are tables
Of values obtained via Hess's Law

$$\Delta G^o_{,rx} = \sum n_i \Delta G^o{}_{f,i,products} - \sum n_i \Delta G^o{}_{fi,reac\,tan\,ts}$$

f means formation at standard state 25 ^{o}C!!!!!

State of Matter	Standard (Reference) State
Solid	Pure solid
Liquid	Pure liquid
Gas	1 atm pressure
Solution	1 M concentration
Elements	) G$_f^o$/ 0

Gibbs Standard Free Energy Example Calc. 1:
What Is the standard free energy change of the
following Reaction? $2\,PbS_s + 3O_{2,g} \rightarrow 2\,PbO_s + 2SO_{2,g}$

Substance	$\Delta G_f{}^0$ (kJ/mole)
PbO	-188.9
SO$_{2(gas)}$	-300
PbS	-99
O$_{2(gas)}$	0

$$\Delta G^o_{rx} = \sum n_i \Delta G^o{}_{f,i,products} - \sum n_i \Delta G^o{}_{fi,reac\,tan\,ts}$$

$$\Delta G^o_{rx} = \{2(-188.9) + 2(-300)\} - \{2(-99) + 3(0)\}$$

$$\Delta G^o_{rx} = \{-377.8 + -600\} - \{-198\}$$

$$\Delta G^o_{rx} = -779.8kJ$$

Gibbs Standard Free Energy Example Calc. 1:
What Is the standard free energy change of the
following Reaction? $2\,PbS_s + 3O_{2,g} \rightarrow 2\,PbO_s + 2SO_{2,g}$

$$\Delta G^o_{rx} = \sum n_i \Delta G^o{}_{f,i,products} - \sum n_i \Delta G^o{}_{fi,reac\,tan\,ts}$$

$$\Delta G^o_{rx} = -779.8kJ$$

For comparison, we calculated from before:

$$\Delta H_{rx} = -832kJ \qquad \Delta S_{rx} = -168\frac{J}{K} \qquad \Delta G_{free\,energy} = -782kJ$$

$$\Delta G_{free\,energy} = -832kJ - T\left(-168\frac{J}{K}\right)$$

$$\Delta G_{free\,energy} = -832kJ - (298K)\left(-168\frac{J}{K}\right)$$
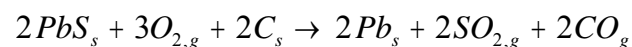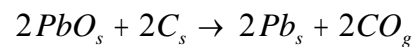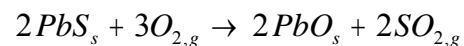
Not too bad of
Agreement!

17

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Module #20
Spontaneity

Summing Reactions

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Rx#		$\Delta G_{reaction}$
1	$A + B \longrightarrow nC$	$\Delta G_{reaction\ 1}$
2	$nC + D \longrightarrow E$	$\Delta G_{reaction\ 2}$
3	$A + B + D \rightarrow E$	$\Delta G_{reaction\ 1} + \Delta G_{reaction\ 2}$

Summing Free Energy Example Calculation Why was lead one of the first **elements** first processed by man? A. Calculate the standard free energy of the Combined reactions. B. Calculate the free energy of the reaction at 600 ºC (campfire temp).

$$2PbS_s + 3O_{2,g} \rightarrow 2PbO_s + 2SO_{2,g}$$

$$2PbO_s + 2C_s \rightarrow 2Pb_s + 2CO_g$$

$$\overline{2PbS_s + 3O_{2,g} + 2C_s \rightarrow 2Pb_s + 2SO_{2,g} + 2CO_g}$$

Summing Free Energy Example Calculation Why was lead one of the first elements first processed by man? A. Calculate the standard free energy of the Combined reactions. B. Calculate the free energy of the reaction at 600 ºC (campfire temp).
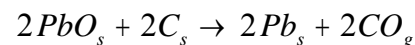
$$2PbS_s + 3O_{2,g} \rightarrow 2PbO_s + 2SO_{2,g}$$

$$\Delta H_{rx}^O = -832kJ \qquad \Delta S_{rx}^0 = -168\frac{J}{K} \qquad \Delta G_{rx}^o = -779.8kJ$$

$$2PbO_s + 2C_s \rightarrow 2Pb_s + 2CO_g$$
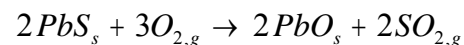
Need standard free energy to solve A

But! Will also need standard enthalpy and S
To solve B – so solve for those

18

Substance	ΔH_f^0 (kJ/mole)	S^0(J/K-mole)
PbS	-100	91
PbO	-219	66.5
Pb	0	0
$O_{2(gas)}$	0	205
$SO_{2(gas)}$	-297	248
C_{solid}	0	0
$CO_{(gas)}$	-110.5	198

$$2PbO_{solid} + 2C_{solid} \longrightarrow 2Pb_{solid} + 2CO_{(gas)} \qquad ?$$

$$\Delta H = [\{(2(0)+2(-110.5)\}-\{2(-219)+2(0)\}] = +217 kJ$$

$$\Delta S = [\{2(0)+2(198)\}-\{2(66.5)+2(0)\}] = 263 J/K$$

$$2PbO_s + 2C_s \rightarrow 2Pb_s + 2CO_g$$

$$\boxed{\Delta H_{rx}^O = 217 kJ} \qquad \boxed{\Delta S_{rx}^0 = 263\frac{J}{K}} \qquad \boxed{\Delta G_{rx}^o = +138.6 kJ}$$

$$\Delta G_{free\ energy} = \Delta H_{rx} - T\Delta S_{rx}$$

$$\Delta G_{free\ energy} = 217 kJ - T\left(263\frac{J}{K}\right)\left(\frac{kJ}{10^3 J}\right)$$

At standard conditions

$$\Delta G^o = 217 kJ - T\left(0.263\frac{kJ}{K}\right)$$

$$\Delta G^o = 217 kJ - (25+273)K\left(0.263\frac{kJ}{K}\right) = +138.6$$

At campfire conditions

$$\Delta G^o = 217 kJ - (873)K\left(0.263\frac{kJ}{K}\right) = -12.56$$

Net reaction at 25 ºC

$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad \Delta G_{rx}$$

$$2PbS_{(solid)} + 3O_{2(gas)} \longrightarrow PbO_{(solid)} + 2SO_{2(gas)} \qquad -779.8\ kJ$$

$$2PbO_{soloid} + 2C_{solid} \longrightarrow 2Pb_{solid} + 2CO_{(gas)} \qquad +138.6 kJ$$

$$2PbS + 3O_{2(gas)} + 2C_{solid} \longrightarrow 2Pb_{solid} + 2SO_{2gas} + 2CO_{gas}$$

$$\textbf{sum} = -641 kJ$$

The net standard free energy for the coupled two reactions is -641 kJ, spontaneous

---

Net reaction at 600 ºC

$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad \Delta G_{rx}$$

$$2PbS_{(solid)} + 3O_{2(gas)} \longrightarrow PbO_{(solid)} + 2SO_{2(gas)} \qquad -685\ kJ$$

$$2PbO_{soloid} + 2C_{solid} \longrightarrow 2Pb_{solid} + 2CO_{(gas)} \qquad -12.6 kJ$$

$$2PbS + 3O_{2(gas)} + 2C_{solid} \qquad 2Pb_{solid} + 2SO_{2gas} + 2CO_{gas}$$

$$\textbf{sum} = -697 kJ$$

The reduction of Pb in PbS to metal and oxidation of S in PbS to sulfur dioxide gas is spontaneous at campfire temperatures of 600ºC
Context point: can manufacture pure lead in a campfire

Slide 1

Context Slide

DUTCH BOY PAINTER
Magazine
Vol. 29 No. 2   1936

Slide 2

Where did all the lead go?   **Context Slide**

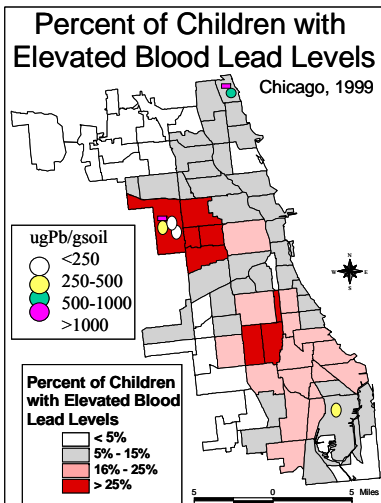| Decade	Estimate lbs white lead/housing unit
1914-23	110
1920-29	87
1930-39	42
1940-49	22
1950-59	7
1960-69	3
1970-1979	1

TiO_2 makes inroads particularly in Europe

White lead restricted

$$\frac{300\,gPb}{10^6\,gsoil}\,x\,\frac{1lbPb}{453.59\,gPb}\,\frac{1.2\,gsoil}{cm^3}\,x\,\frac{228.44mi^2}{Chicago}\,x\left[\frac{1.609km}{mi}\right]^2 x\left[\frac{10^5\,cm}{km}\right]^2 x3cm = \boxed{14,790,239\,lbPb}$$

300ppm = "background" level of Chicago soil lead

Depth: does
Not move down
Because of Oh Card me PleaSe

Slide 3

Percent of Children with Elevated Blood Lead Levels
Chicago, 1999

ugPb/gsoil
○ <250
○ 250-500
○ 500-1000
○ >1000

Percent of Children
with Elevated Blood
Lead Levels
■ < 5%
■ 5% - 15%
■ 16% - 25%
■ > 25%

5   0   5 Miles

Context Slide
Relates to
a) Age of Housing
b) "Gentrification"

Relevant Chem 102 Concepts:
1. Temperature dependence of spontaneous reactions
2. Stability of soil lead form (Oh Card me PleaSe)

Slide 4

"A" students work
(without solutions manual)
~ 10 problems/night.

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**Module #20
Spontaneity**

**Relating Free Energy
To Concentrations**

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20

The free energy of the reaction related to
    a) standard free energy change
    b) and the ratio of concentrations of
products to reactants, Q

$$\boxed{\Delta G = \Delta G^o + RT \ln Q}$$

In this equation you can use (simultaneously)
    Pressures
    Concentrations
The ln(Q) is treated as unitless

Free Energy and Conc. Example Calc. Calculate the free energy of the reaction if the partial pressures of the gases are each 0.1 atm, 298 K. Remember, we calculated ΔG_{rx} to be -641 kJ at 298K (25 °C)

$$2PbS_{(s)} + 3O_{2(s)} + 2C_{(s)} \Leftrightarrow 2Pb_{(s)} + 2SO_{2(g)} + 2CO_{(g)}$$
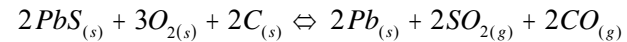
$$\Delta G = \Delta G^o + RT \ln Q$$

$$\Delta G_{rx} = -641kJ + \left(8.314\frac{J}{K}\right)(298K)\ln\left(\frac{[Pb_s]^2 P_{SO_2}^2 P_{CO}^2}{[PbS_s]^2 P_{O_2}^3 [C_s]^2}\right)$$

$$\Delta G_{rx} = -641kJ + (2477.57J)\ln\left(\frac{[1]^2 P_{SO_2}^2 P_{CO}^2}{[1]^2 P_{O_2}^3 [1]^2}\right) \qquad \Delta G_{rx} = -641kJ + (2.47757kJ)\ln(0.1)$$

$$\Delta G_{rx} = -641kJ + (2.47757kJ)\ln\left(\frac{P_{SO_2}^2 P_{CO}^2}{P_{O_2}^3}\right) \qquad \Delta G_{rx} = -641kJ + (2.47757kJ)(-2.302)$$

$$\Delta G_{rx} = -641kJ + (-5.703kJ)$$

$$\Delta G_{rx} = -641kJ + (2.47757kJ)\ln\left(\frac{0.1_{SO_2}^2 \, 0.1_{CO}^2}{0.1_{O_2}^3}\right)$$

$$\boxed{\Delta G_{rx} = -647\frac{kJ}{mol}}$$

When Q = K (equilibrium): $\Delta G = \Delta G^o + RT \ln Q$

$$0 = \Delta G^o + RT \ln K$$

$$- RT \ln K = \Delta G^o$$

$$\boxed{\Delta G^o = - RT \ln K}$$

At equilbrium no
Energy to drive
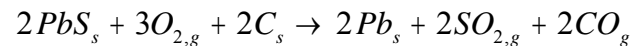Rx one way or other

K = 1	-RT ln (1) = 0
K >1	-RT ln (>1) = -(+) < 0
K < 1	-RT ln (<1) = -(-) > 0

Example Problem 2 Free Energy and Equilibrium:
What is the equilibrium constant for the reaction at a campfire temperature?

$$2PbS_s + 3O_{2,g} + 2C_s \rightarrow 2Pb_s + 2SO_{2,g} + 2CO_g$$

$$\boxed{\Delta G^o = - RT \ln K}$$

$$\frac{\Delta G^o}{- RT} = \ln K$$

$$e^{\frac{-\Delta G^o}{RT}} = K$$

ΔG° = -697kJ/mol rx

$$K = e^{\frac{-\left(-697\frac{kJ}{mol}\right)}{\left(8.314x10^{-3}\frac{kJ}{mol\,K}\right)298K}}$$
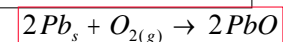
$$K = e^{281} > 10^{100}$$

Example 3 Free Energy and Equilibrium:
The corrosion of Fe at 298 K is $K = 10^{261}$.
What is the equilibrium constant for corrosion of lead?

$$2Pb_{solid} + O_{2gas} \longrightarrow 2PbO_{solid}$$
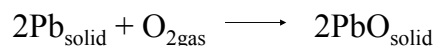
We don't have any K values so we need
To go to appendix for various enthalpy and
Entropies to come at K from the backside

Substance	ΔH_f^0 (kJ/mole)	S^0(J/K-mole)
PbS	-100	91
PbO	-219	66.5
Pb	0	0
$O_{2(gas)}$	0	205
$SO_{2(gas)}$	-297	248
C_{solid}	0	0
$CO_{(gas)}$	-110.5	198

$$2Pb_s + O_{2(g)} \rightarrow 2PbO$$

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

$\Delta H^o = 2(-219) - \{2(0) + 2(0)\} = $ -438kJ

$\Delta S^o = 2(.0665) - \{2(0) + 2(.205)\} = $ -0.277kJ/K

$\Delta G^o = $ -438 - T(-.277) = -438 - (298)(-0.277) = -355kJ

RT ln K = - ΔG^o $\Delta G = -355kJ$

$$K = e^{\frac{-\Delta G^0}{RT}} = e^{\frac{-\left(-355\frac{kJ}{mol}\right)}{\left(8.314x10^{-3}\frac{kH}{mol\,K}\right)298K}}$$

$K = e^{143} > 127x10^{62}$

K for rusting of Fe = 10^{261}
K for rusting of Pb = $1.27x10^{62}$

so: even though the reaction is favorable
it is less so than for iron.
Lead rusts less than iron = used for plumbing

**Module #20
Spontaneity**

What you need to
know

1. Be able to rank the entropy of various phases of materials, including allotropes
2. Be able to rank the entropy of various compounds
3. Explain entropy concepts as related to chemical geometry
4. Calc. standard entropy change for a reaction
5. Relate surrounding entropy to reaction enthalpy
6. Calc. temperature at which a reaction becomes spontaneous
7. Explain why TiO_2 was relatively late in replacing $PbCO_3$ as a white pigment; why lead was one of first pure metals obtained by humanity
8. Convert standard free energy to equilibrium constant

"A" students work (without solutions manual) ~7 problems/night.

**Module #20
Spontaneity**

END