Chem 1B Objective 12:
Predict whether a reaction occurs using thermodynamics.

Key Ideas: Does a reaction occur? Some reactions occur spontaneously; others do not.

ΔG is the criterion used to predict whether a reaction occurs spontaneously: $\Delta G < 0$ means spontaneous reaction.
Enthalpy and Entropy determine whether a reaction occurs spontaneously.

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

Compare ΔH and ΔS. Determine T at which reaction occurs or not.

ΔG is related to K_{eq}: $\Delta G = -RT \ln K_{eq}$
where R = gas constant = 8.31 J/mole K and T = temperature in K.

Objective: What type of energy is contained in matter?

1. If a rock and gold cup don't contain heat, what type of energy does each object contain?

2. Most reactions are:

(i) exothermic (ii) endothermic (iii) neither

3. Compare a gas to a liquid to a solid.

a. Which phase has the most entropy? Why?

b. For most processes, ΔS is:

(i) > 0 (ii) < 0 (iii) $= 0$

c. Does steam contain entropy?

Energy Types are classified as Thermodynamic or Non-Thermodynamic

<u>Internal Energy</u> = E = energy inside atoms and molecules
<u>Enthalpy</u> = H = that part of Internal Energy that is converted into heat
<u>Heat</u> = q = transfer of energy from one object to another due to a difference in temperature
<u>Work</u> = w = the ability to move matter

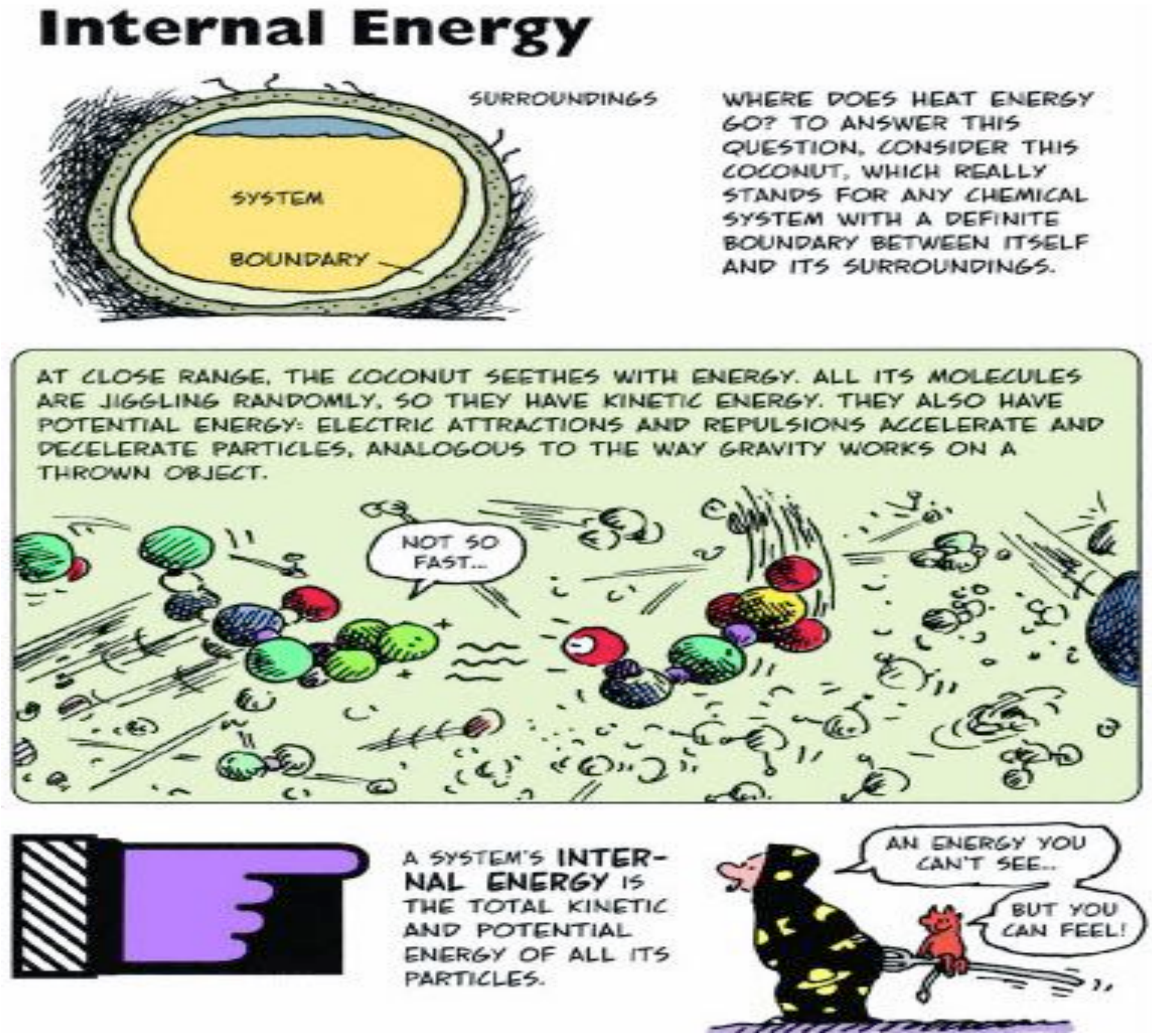
<u>A Substance Contains Internal Energy and Enthalpy</u>
(thermodynamic quantities)
<u>But Not Heat or Work</u> (non-thermodynamic quantities)

<u>Internal Energy and Enthalpy</u> (thermo quantities) ***<u>cannot</u>*** **<u>be directly measured</u>**
<u>but Heat and Work</u> (non-thermo quantities) ***<u>can</u>***.

Table. Thermodynamic vs. Non-Thermodynamic Quantity Comparison

Thermodynamic Quantity (State Functions)	Non-Thermodynamic Quantities (Path Functions)
Property of A Substance	*Not* A Property of A Substance
A Substance Contains A Thermo Quantity	A Substance Does Not Contain A Non-Thermo Quantity
Cannot be directly measured	Can be directly measured
Internal Energy: $\Delta E = q + w$	Work = $w = - p \Delta V$
Enthalpy (Exothermic/Endothermic): $\Delta H = q$	Heat = $q = ms \Delta T$
Entropy: $\Delta S \geq q/T$	
Free Energy: $\Delta G = \Delta H - T \Delta S$	

Quantify Internal Energy and Enthalpy (thermo properties) **by Measuring Heat and Work** (non-thermo properties)



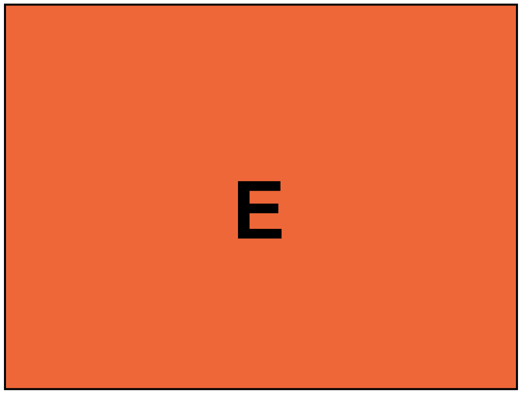
The Cartoon Guide to Chemistry, by Larry Gonick and Craig Criddle, HarperCollins, 2005, 249 pages, $16.95 (ISBN 0-06-093677-0)

***Enthalpy* and *Entropy* are the 2 Driving Forces of a Reaction**

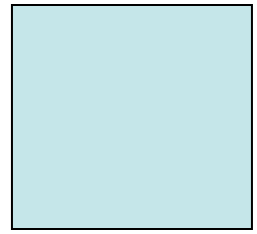
Enthalpy = H = that part of Internal Energy that is converted into heat

$$\boxed{\Delta H = q}$$

Most reactions are **EXOTHERMIC**!



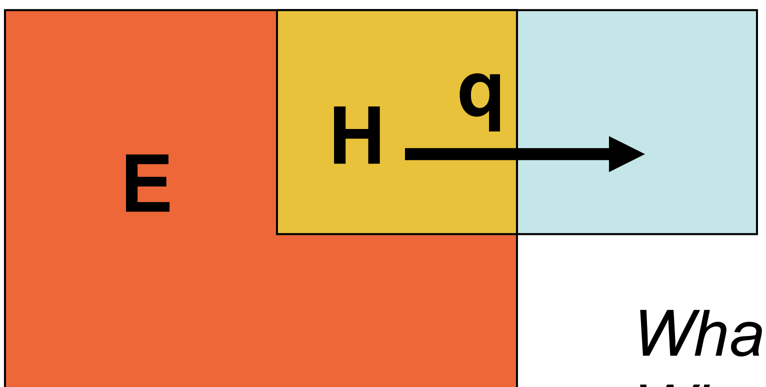
Hot object (gold cup in parking lot)
Contains internal energy



Hot object touches Cold object

Part of E becomes H

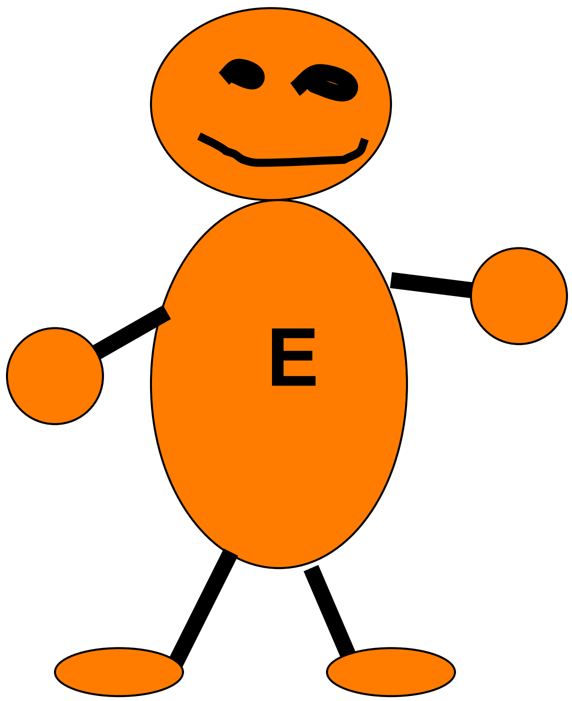
H is converted to q ==> q transferred!



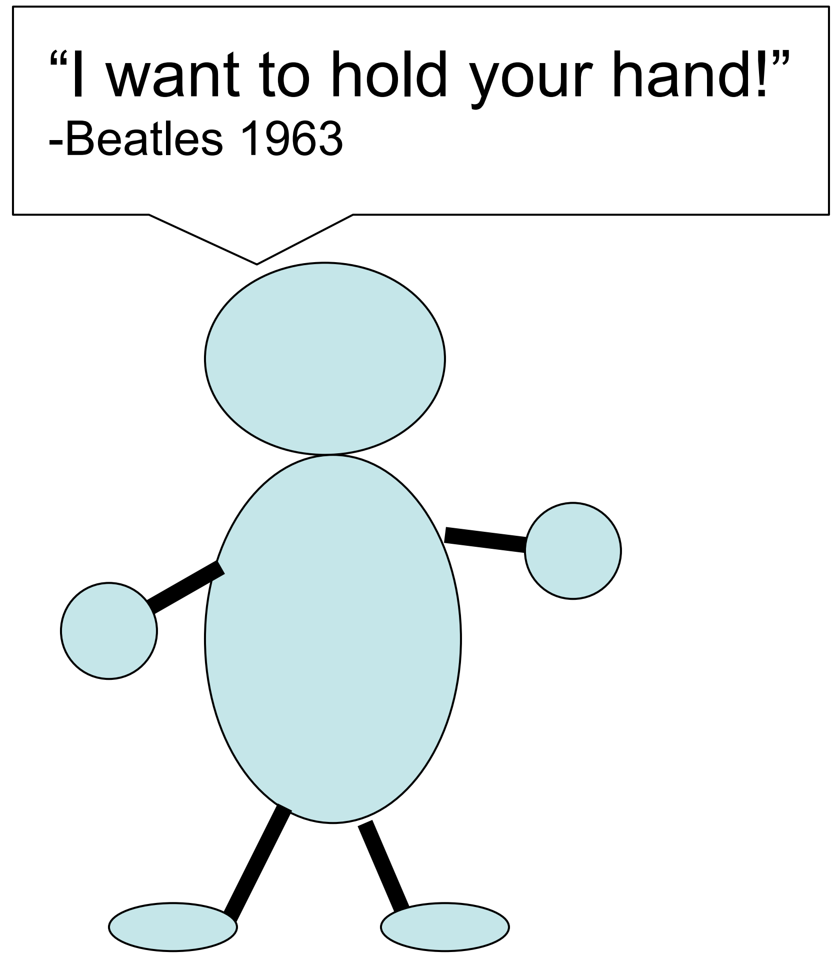
Cold object

What happens to E?
What happens to Temperature of each object?

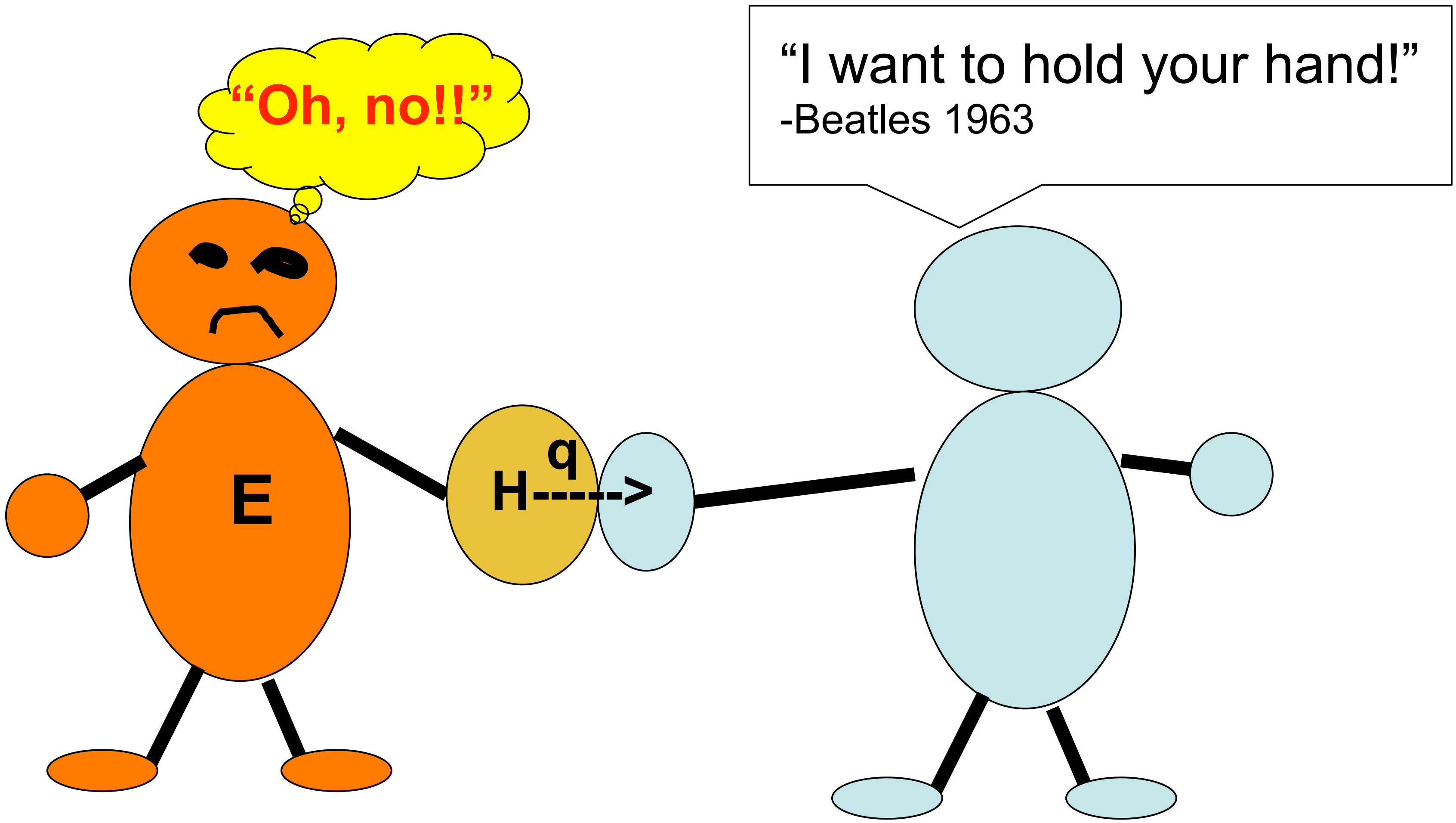
Hot object



Hot object
Contains internal energy



Cold object



Hot object touches Cold object

Part of E becomes H

H is converted to q ==> q transferred!

so **ΔH = q**

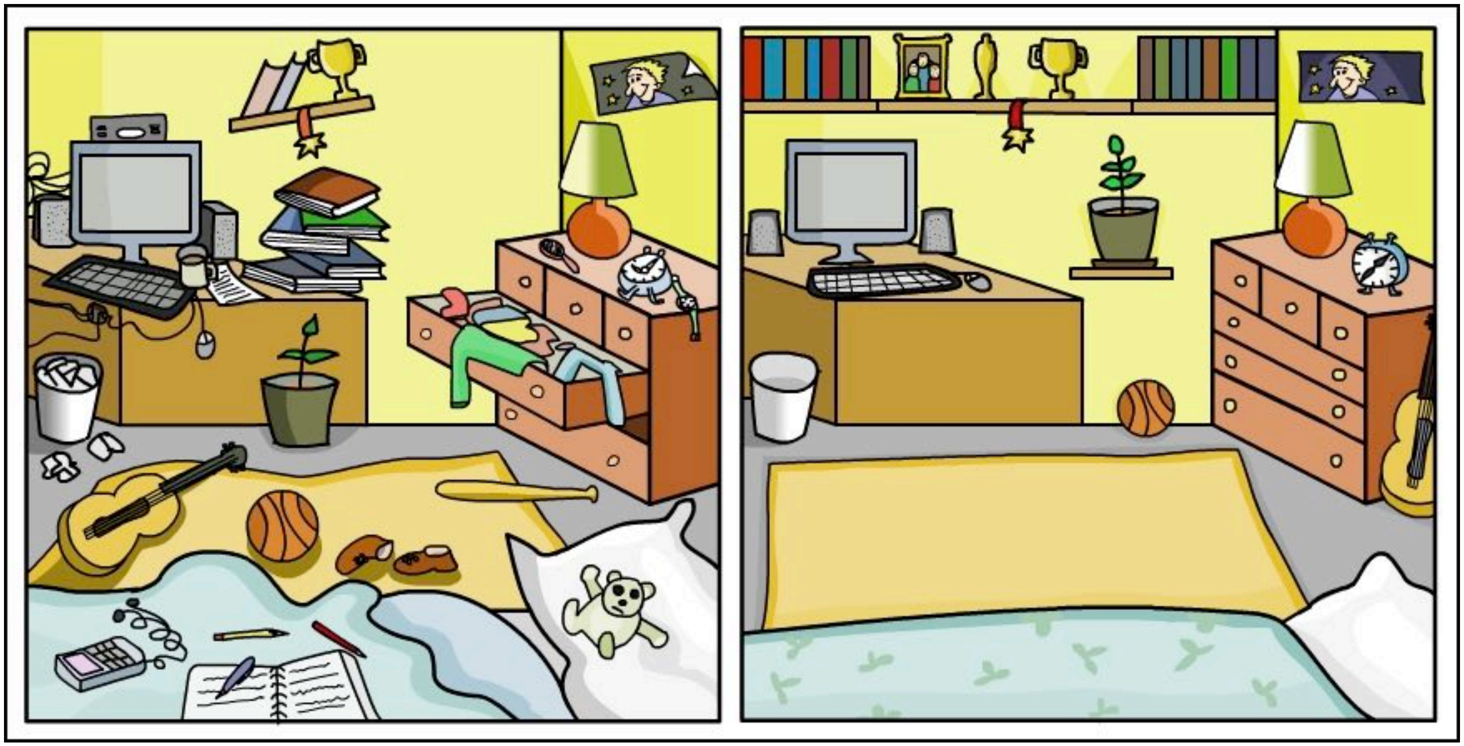
***Enthalpy* and *Entropy* are the 2 Driving Forces of a Reaction**

Entropy = *S* = *Tells Us the Amount of Disorder* (or Order) *In A System*

$$\boxed{\Delta S \geq q/T}$$

Entropy = disorder = chaos

$\Delta S > 0, < 0,$ or $=0$?



$\Delta S > 0, < 0,$ or $=0$?

http://lessmess.com.au/blog/just-for-fun/messy-neat-room/

Entropy (S) refers to the Dispersal Of Energy

Nature: ***Things want to be at low energy.***

It takes energy to keep things ordered.

The Entropy of the Universe is ______.

What happens when you can't hold back the door?

http://www.secondgearsports.com/blog

Is energy being dispersed?

Is $\Delta S > 0$ or < 0?

http://fineartamerica.com/featured/1-girl-popping-a-balloon-ted-kinsman.html

Entropy = dispersal of energy

Which *state of matter* has the highest entropy?

$\Delta S > 0, < 0,$ or $=0$?

http://www.bubblews.com/news/250985-ice-cubes

http://fitsystemsatx.com/2012/12/water-vs-coke/

http://whatscookingamerica.net/boilpoint.htm

Entropy refers to the Dispersal of Energy.

Gas has the **most** entropy. Solids the **least** entropy.

For most processes, $\Delta S > 0$

Steam contains **ENTROPY**!

Physical Processes and Chemical Reactions involve Entropy

Without doing a calculation, what is ΔS for each reaction?

(i) > 0

(ii) < 0

(iii) = 0

H_2O (l) -----> H_2O (g)

C_2H_6 (g) + 3.5 O_2 (g) ---> 2 CO_2 (g) + 3 H_2O (g)

A Reaction That Starts and Continues to Occur Is a ***Spontaneous Reaction***

Which process is Spontaneous?

A

B

http://www.acordceo.org/2008/03/

Objective: Determine whether a reaction occurs spontaneously.

Burning wood:
wood + O_2 ---> CO_2 + H_2O

http://syncora.blogspot.com/2011/05/its-been-long-time-since-i-had-vivid.html

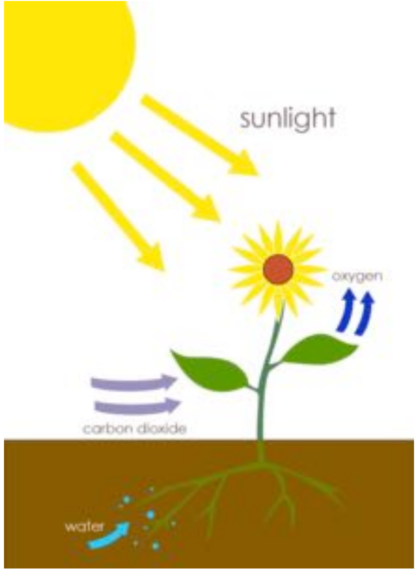
Dissolution of NaCl:
NaCl (s) ---> Na^+ (aq) + Cl^- (aq)

http://www.pdesas.org/module/content/resources/15110/view.ashx

Photosynthesis:
CO_2 + H_2O ---> food + O_2

Boiling water: H_2O (l) ---> H_2O (g)

http://whatscookingamerica.net/boilpoint.htm



https://en.wikipedia.org/wiki/Photosynthesis

The Driving Forces (H and S) ***tell us whether a Reaction Occurs or Does Not Occur.***

Change in Free energy (ΔG) relates ΔH and ΔS:

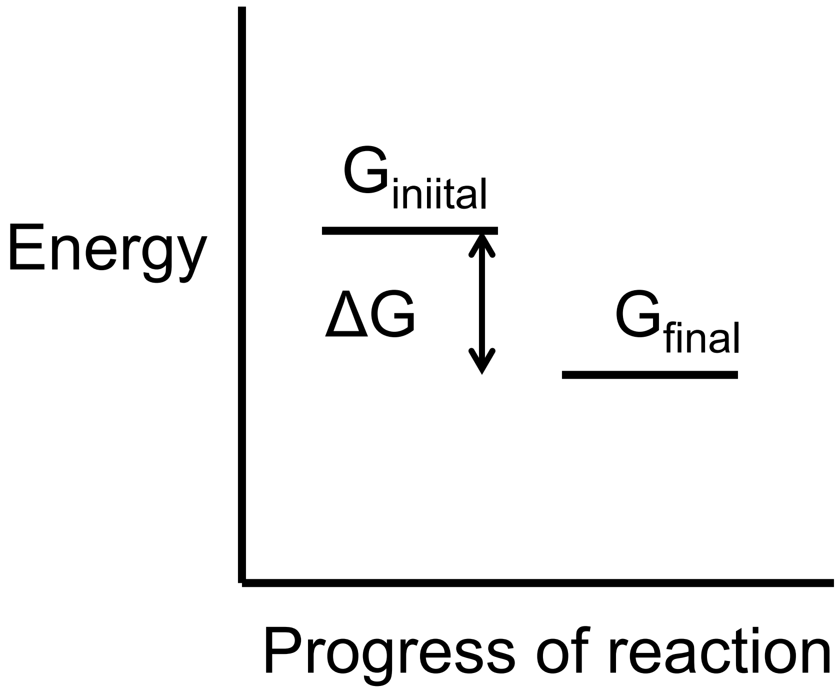
$$\Delta G = \Delta H - T\Delta S$$

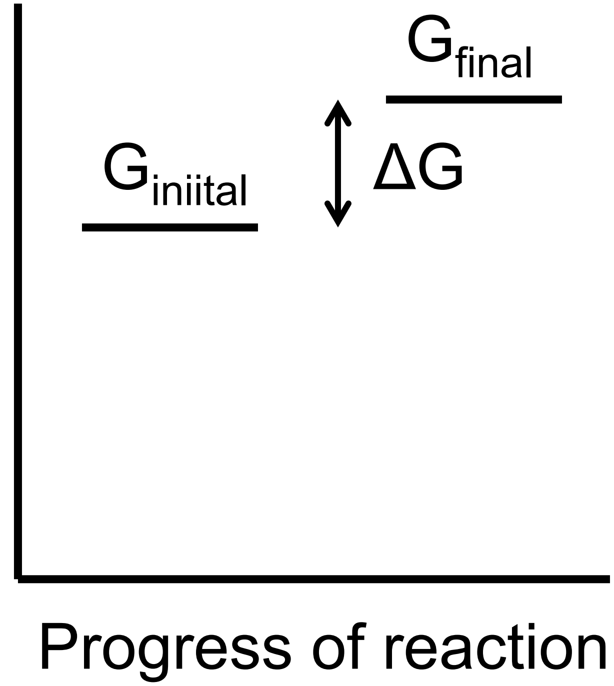
Use ΔG to Predict Whether A Reaction Occurs Spontaneously

If $\Delta G > 0$ **not** spontaneous
If $\Delta G < 0$ spontaneous

Burning wood is spontaneous ($\Delta G < 0$)
Photosynthesis is not spontaneous ($\Delta G > 0$)

Dissolution of NaCl is spontaneous ($\Delta G < 0$)
Boiling water is not spontaneous ($\Delta G > 0$)





$\Delta G < 0$
Extra Energy lost
Spontaneous

$\Delta G > 0$
Extra Energy had to be put **into** system
Not Spontaneous

Objective: Use **Hess' law** to Calculate Δ H, ΔG, and ΔS. See Appendix 2.

How does *each driving force* (ΔH and ΔS) and T contribute to make a reaction spontaneous? (4 cases of ΔH and ΔS)

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

Case	Δ H	ΔS	ΔG (> or < 0)	Any *or* Some *or* No Temperature
1	> 0	> 0		Rxn occurs at _____ T
2	> 0	< 0		Rxn occurs at _____ T
3	< 0	> 0		Rxn occurs at _____ T
4	< 0	< 0		Rxn occurs at _____ T

NOTE: Assume ΔH and ΔS do **not** change with T
But ΔG **does** change with T.

A Reaction Can Be "***Favored***" by Enthalpy or Entropy or Both.
Favored Means Helping the Reaction Occur Spontaneously

A reaction is favored by enthalpy when ΔH is

(i) > 0 (ii) < 0 (iii) $= 0$

A reaction is favored by entropy when ΔS is

(i) > 0 (ii) < 0 (iii) $= 0$

Can you (*scientist*) make a ***spontaneous*** reaction not occur?
Can you (*scientist*) make a ***non-spontaneous*** reaction occur?

YES!!

Use $\Delta G = \Delta H - T\Delta S$ to determine a T at which a reaction occurs or not occurs.

Objective: Determine T at which a reaction occurs/not occurs

Methane combustion:

CH_4 (g) + 2 O_2 (g) --> CO_2 (g) + 2 H_2O (g)

*Can you make methane **NOT** combust?*

ΔH = -802 kJ/mole Favored by Enthalpy

ΔS = -5.2 J/mole K **NOT** Favored by Entropy

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

At 25^{o}C: ΔG = -802,000 J/mole - (298)(-5.2 J/mole K)

= -800,450 J/mole ==> ***spontaneous***!

At what T is $\Delta G > 0$?

0 = -802,000 J/mole - (T)(-5.2 J/mole K)

T = 154,230 K

At T greater than 154,230 K, methane does **not** combust!

Objective: Determine T at which a reaction occurs/not occurs

Methane combustion:

$$CH_4\ (g) + 2\ O_2\ (g) \dashrightarrow CO_2\ (g) + 2\ H_2O\ (g) + \text{heat}$$

*Can you make methane **NOT** combust?*

$\Delta H = -802$ kJ/mole Favored by Enthalpy

$\Delta S = -5.2$ J/mole K **NOT** Favored by Entropy

At 25^{o}C: $\Delta G = -802{,}000$ J/mole - (298)(-5.2 J/mole K)

= -800,450 J/mole ==> ***spontaneous***!

At T greater than 154,230 K, methane does **not** combust!

Remember Equilibrium:

Add heat (increase T) and reaction shifts to reactant side.

This calculation supports LeChatelier's principle.

Objective: Determine T at which a reaction occurs/not occurs

Melting Ice: H_2O (l) --> H_2O (s)

Can you make Water Freeze?

ΔH = - 6.01 kJ/mole Favored by Enthalpy

ΔS = - 22.0 J/mole K NOT Favored by Entropy

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

At 25°C: ΔG = -6,010 J/mole - (298)(-22.0 J/mole K)

= +546 J/mole ==> NOT ***spontaneous***!

At what T is $\Delta G < 0$?

0 = -6,010 J/mole - (T)(-22.0 J/mole K)

T = 273 K

At T less than 273 K, water does freeze!

Objective: Determine T at which a reaction occurs/not occurs

Melting Ice: H_2O (l) --> H_2O (s)

Can you make Water Freeze?

ΔH = - 6.01 kJ/mole Favored by Enthalpy

ΔS = - 22.0 J/mole K NOT Favored by Entropy

At 25^{o}C: ΔG = -6,010 J/mole - (298)(-22.0 J/mole K)

= +546 J/mole ==> NOT ***spontaneous***!

At T less than 273 K, ice does melt!

Remember Equilibrium:

Add heat (increase T) and reaction shifts to product side.
This calculation supports LeChatelier's principle.

You Can Make A Non-spontaneous Reaction Occur By Changing The Temperature!

Equilibrium: K_{eq} tells you the relative amounts of products and reactants.

Objective: relate ΔG to K_{eq}

A reaction that occurs means K_{eq}:

a. <1 b. $=1$ c. >1

A reaction that occurs means ΔG:

a. <0 b. $=0$ c. >0

$$\boxed{\Delta G = -RT \ln K_{eq}}$$

Objective: relate ΔG to K_{eq}

$CH_3COOH \Longleftrightarrow H^+ + CH_3COO^-$ $K_a = 1.8 \times 10^{-5}$

We know acetic acid is a weak acid. Give reasons.
What is ΔG for this reaction?

$\Delta G = -RT \ln K_{eq} = -(8.31 \text{ J/mole K})(298 \text{ K}) \ln (1.8 \times 10^{-5})$

$= 27{,}100$ J/mole ===> non-spontaneous

Is acetic acid a stronger or weaker acid at T = 80°C?

Calculate K at 80°C to support your answer.

Objective: relate ΔG to K_{eq}

$CH_3COOH \Longleftrightarrow H^+ + CH_3COO^-$ $K_a = 1.8 \times 10^{-5}$

Acetic acid is a weak acid. $\Delta G = 27{,}100$ J/mole => non-spontaneous
Is acetic acid a stronger or weaker acid at T = 80°C?

Calculate K at 80°C to support your answer.
Use $\Delta G = \Delta H - T\Delta S$ and $\Delta G = -RT \ln K_{eq}$
$\Delta H = -1.8$ kJ/mole, $\Delta S = -166$ J/mole K
At T = 80°C = 353 K, $\Delta G = (-1800 \text{ J/mole}) - (353)(-166 \text{ J/mole K})$
$= 56{,}800$ J/mole

$$56{,}800 \text{ J/mole} = -(8.31 \text{ J/mole K})(353 \text{ K}) \ln (K_a)$$

At T = 80°C, $K_a = 3.9 \times 10^{-9}$ ===> weaker acid!

Equilibrium: heat is a product so increase T and reaction shifts to reactant side.

Lab 7. Part C. Make a Non-Spontaneous Reaction Occur By Changing Temperature

Does Baking Soda Decompose Spontaneously at room temperature?

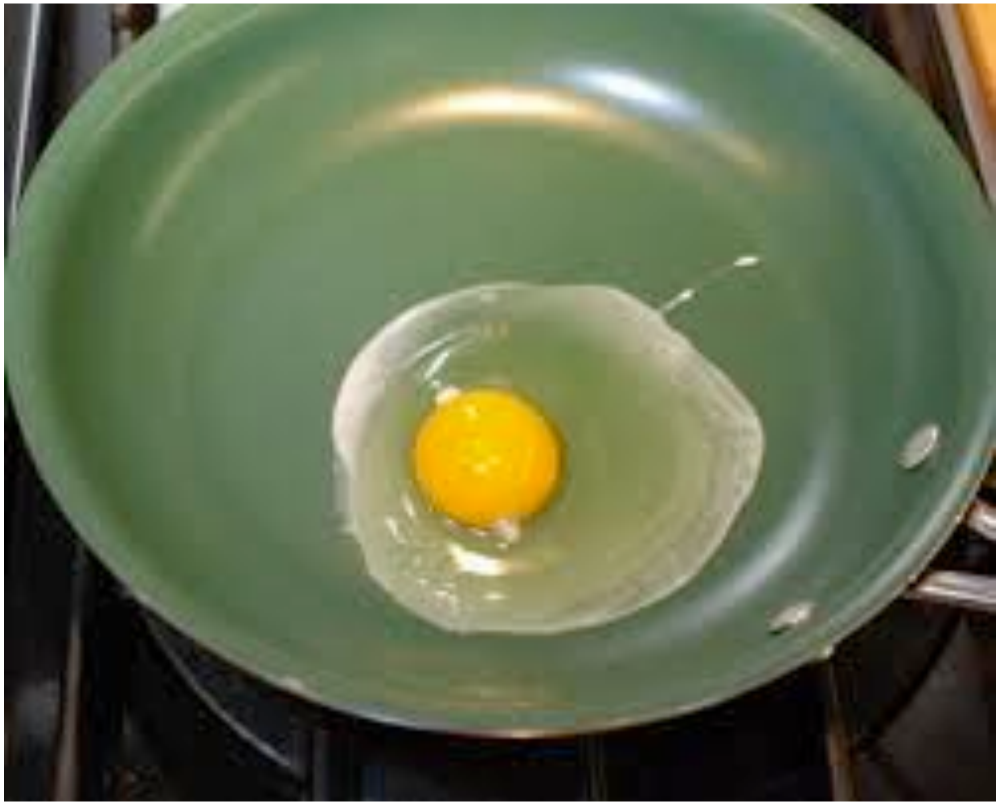
$$NaHCO_3\ (s) \text{ ---> } Na_2CO_3\ (s) + H_2O\ (g) + CO_2\ (g)$$

Calculate ____ to find out.

If Baking Soda does not decompose at room temperature, at what temperature will it decompose?

Lab 7. Part C. Make a Non-Spontaneous Reaction Occur

Does an egg cook by itself?

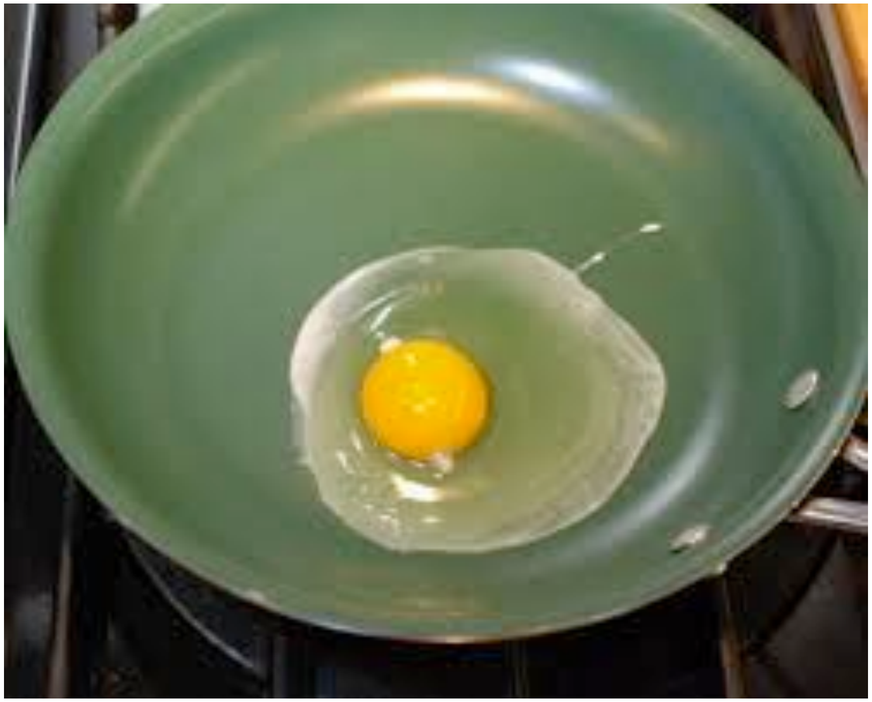


http://www.examiner.com/review/is-orgreenic-cookware-a-scam

How can you cook at egg?

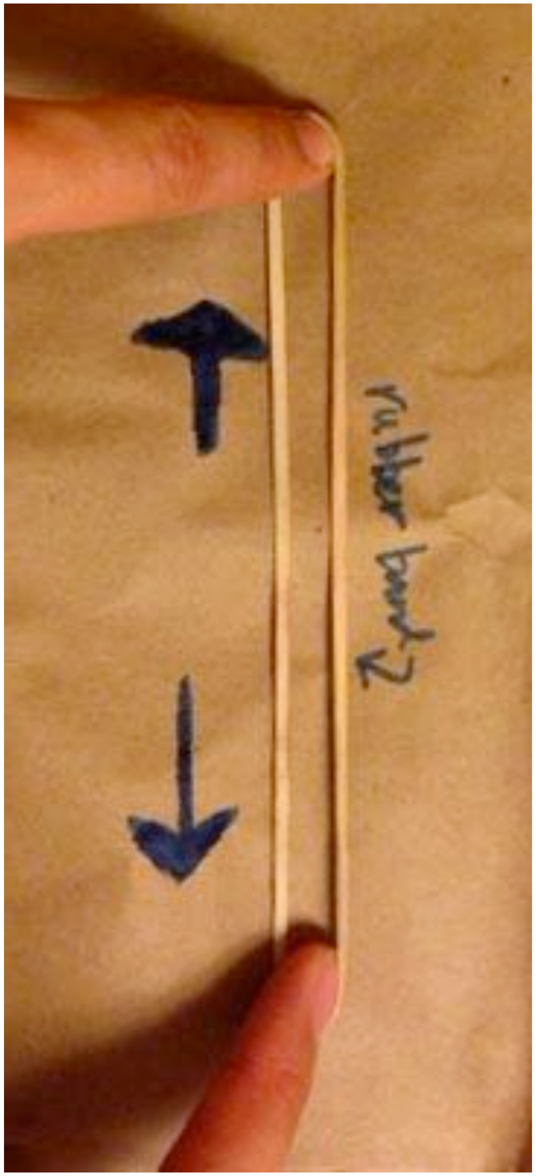
Lab 7. Part C. Make a Non-Spontaneous Reaction Occur

How is cooking an egg like breaking a stick?



http://www.examiner.com/review/is-orgreenic-cookware-a-scam

Lab 7. Part D. Bungee Jumper!



http://www.picgifs.com/sport-graphics/bungee-jumping/sport-graphics-bungee-jumping-159335-950323/

https://www.quora.com/What-is-happening-on-the-molecular-level-when-you-stretch-a-stretchy-object-such-as-a-rubber-band

Objective: Use thermo to determine Storage Temperature
(and Shelf Life)

Ammonia, NH_3, is a base and is used to make fertilizer.
Does NH_3 decompose at room temperature?
At what temperature should be NH_3 be stored?

$$2\ NH_3\ (g) \longrightarrow N_2\ (g) + 3\ H_2\ (g)$$

What does ΔG or K_{eq} tell you? (ΔG = 33 kJ, $K_{eq} = 1.9\times10^{-6}$)
What does ΔH tell you? (ΔH = 91 kJ)
Increasing T shifts the (equilibrium) reaction to the ______.
Does K_{eq} increase or decrease if temperature increases?
How can you make NH_3 decompose slower?

You Can Make A Non-spontaneous Reaction Occur By Changing The Temperature!

Another way to make a non-spontaneous reaction occur is to use the energy (ΔG) from a spontaneous reaction.

$$
\begin{array}{lll}
A + B \rightarrow C & \Delta G_1 = 10\text{ kJ} \quad \text{non-spontaneous} & (\text{or } K_1) \\
\underline{C \rightarrow D} & \Delta G_2 = -20\text{ kJ} \quad \text{spontaneous} & (\text{or } K_2) \\
A + B \rightarrow D & \Delta G_3 = \Delta G_1 + \Delta G_2 & (K_3 = K_1 K_2) \\
 & \quad\;\; = 10 + (-20) = -10\text{ kJ} &
\end{array}
$$

Overall reaction is Spontaneous!

Objective: How to dissolve an insoluble solid

Insoluble Carbonates and Hydroxides Are Soluble In Acid

I can’t get these *&# lime stains off with water!
This reaction is not spontaneous? Why?

$Ca(OH)_2$ (s) <===> Ca^{2+} (aq) + 2 OH^- (aq)

$K_{sp} = 4.7\text{x}10^{-6}$, ΔG =

How can you use this reaction to make the previous reaction occur?

2 H^+ (aq) + 2 OH^- (aq) <===> 2 H_2O (l) $K = 1\text{x}10^{28}$, ΔG =

See Practice Problems.

Biology: Our body metabolizes glucose by Glycolysis.
1st step of glycolysis, glucose is phosphorylated to glucose 6-phosphate:

glucose + P_i -----> glucose 6-phosphate + H_2O

ΔG = 3.3 kcal/mole ===> non-spontaneous

(where P_i is orthophosphate, HPO_4^{2-})

Use the energy from ATP hydrolysis to make the above reaction occur.

ATP + H_2O -----> ADP + P_i + H^+ ΔG = -7.3 kcal/mole
spontaneous

b. Add the 2 reactions:

glucose + $\cancel{P_i}$ + ATP + $\cancel{H_2O}$ ---> glucose-6-phosphate + $\cancel{H_2O}$ + ADP + $\cancel{P_i}$ + H^+

ΔG = 3.3 + (-7.3) = -4.0 kcal/mole ===> spontaneous

“*High Energy Phosphate Bond*” (BIOLOGY)
To Break a Bond **REQUIRES** Energy
When a Bond Forms, Energy is **RELEASED**

Bond	ΔH, kJ/mole	Bond	ΔH , kJ/mole
P-O	335	P-H	322
P=O	544		
N-O	201	N-H	386
N=O	607		
C-O	358	C-H	411
C=O	799	O-H	459

http://www.wiredchemist.com/chemistry/data/bond_energies_lengths.html

Look at the chemical reaction, not just the bond

The 3 laws of thermodynamics are:
1. energy is neither created nor destroyed,
2. the total entropy in the universe is increasing,
3. a substance at 0K has an entropy of 0.

Ginsberg's restatement of the three laws of thermodynamics:
You can't win.
You can't break even.
You can't quit.

Compare Ginsberg's restatement of the three laws of thermodynamics to the statement of the three regular laws of thermodynamics. Relate each restatement to one of the laws of thermodynamics (one restatement per law; don't use the same law twice). Explain how each restatement relates to the actual law.
Example: Chang, 5th ed., Problem 6.104a and b

We can determine whether a reaction occurs by:
(i) ΔH (ii) ΔG (iii) K_{eq} (iv) k

We can determine how fast a reaction occurs by:
(i) ΔH (ii) ΔG (iii) K_{eq} (iv) k

We can determine the the amount of products formed (related to % yield) by:
(i) ΔH (ii) ΔG (iii) K_{eq} (iv) k

A large K_{eq} means ΔG is:
(i) = 0 (ii) > 0 (iii) < 0 (iv) k

As temperature increases:
(i) k increases (ii) K_{eq} increases (iii) ΔG increases (iv) it is hotter