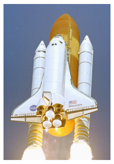
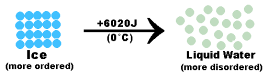
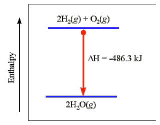
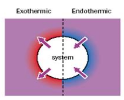
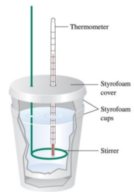
THERMOCHEMISTRY











Thermodynamics

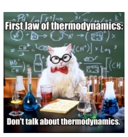
Study of energy and its interconversions

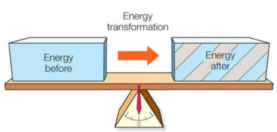
- Energy is TRANSFORMED in a chemical reaction (POTENTIAL to KINETIC)
- HEAT (energy transfer) is also usually produced or absorbed
  - -SYSTEM: part of the universe being studied
  - -SURROUNDINGS: everything else

First Law of Thermodynamics

TOTAL ENERGY IN THE UNIVERSE IS CONSTANT…

Energy cannot be created or destroyed but it can be converted or transformed!



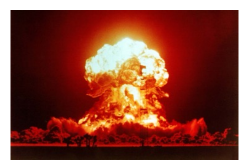


AKA Law of Conservation of Energy

Energy

Ability to produce change or do work

- Joule (J) is the SI unit for energy
- Another common unit is calorie (cal)
- 1 calorie = 4.184 Joules
- 1 kilocalorie = 1000 calories



Energy

Ability to produce change or do work

POTENTIAL ENERGY

- Stored energy from the interactions of charged particles
- Increases with charge or decreases with diameter

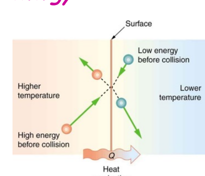
KINETIC ENERGY

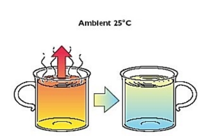
- Energy of motion that depends on mass and speed: $KE = \frac{1}{2}mv^2$
- Greater the mass or speed, more KE of an object

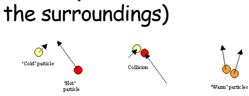
Heat (q)

Quantity of thermal energy

- Heat transfers spontaneously from a warmer object to a colder one (energy transfer)
- Due to molecular collisions… Faster moving particles collide with slower moving ones and transfer some of their energy, changing the speed of both molecules (can also be transferred to the surroundings)







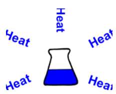
Heat Transfer

EXOTHERMIC

Energy is released (exits) / Feels warm

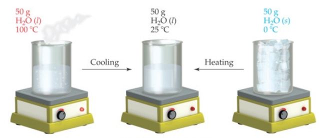
ENDOTHERMIC

Energy is absorbed (enters) / Feels cold



State Functions

Depend only on the change between the initial and final states of a system, not on the process by which the change occurs



- Ex: Adding a catalyst has no effect on the overall energy change
- Enthalpy (ΔH), entropy (ΔS), and free-energy (ΔG) are all state functions

Standard State Conditions

- When quantities given on a test, they are given under these conditions
- Indicated by a little superscript circle (°)

$\Delta H = \Delta H^\circ$

$\Delta S = \Delta S^\circ$

$\Delta G = \Delta G^\circ$

-All gases are at 1 atm

-All liquids and solids are pure

-All solutions are at 1 M

-Energy of formation of an element in its normal state is defined as zero

-Temperature used is room temperature (25°C)

Enthalpy (H)

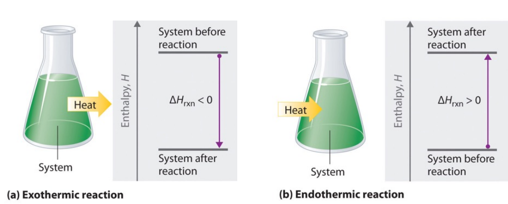
Flow of energy (HEAT EXCHANGE) at constant pressure when two systems are in contact

UNITS ARE TYPICALLY kJ/mol!!

Enthalpy (H)

Flow of energy (HEAT EXCHANGE) at constant pressure when two systems are in contact

- Heat RELEASED (Exo) = NEGATIVE values
- Heat ABSORBED (Endo) = POSITIVE values



Enthalpy (H)

Flow of energy (HEAT EXCHANGE) at constant pressure when two systems are in contact

- Enthalpy of Reaction (ΔH_{rxn}): heat released or absorbed by a reaction (kJ/mol)
- Enthalpy of Formation (ΔH_f): heat released or absorbed when ONE MOLE of a compound is formed from elements
- Enthalpy of Fusion (ΔH_{fus}): heat absorbed to melt (overcome IMFs) of ONE MOLE of solid
- Enthalpy of Vaporization (ΔH_{vap}): heat absorbed to boil (overcome IMFs) of ONE MOLE of liquid

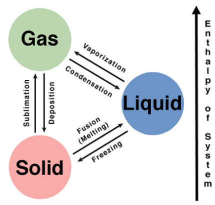
Also known as "HEAT OF…"

IMFs

Don't forget that phase changes always involve the overcoming of IMFs not the breaking of bonds!!

Fusion (melting), vaporization, and sublimation REQUIRE AN INPUT OF ENERGY to overcome the IMFS

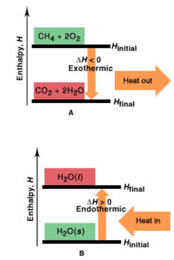
Freezing, condensation, and deposition RELEASE ENERGY as IMFs form



Enthalpy Change (ΔH)

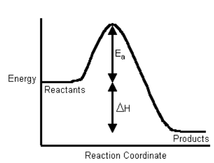
Difference between the potential energies of the products and reactants

- State function
- ΔH = q at constant pressure
- Can be calculated in different ways:
  - -Stoichiometry
  - -Calorimetry (next lesson)
  - -Tables of Standard Values
  - -Hess's Law
  - -Bond Energy (been there)

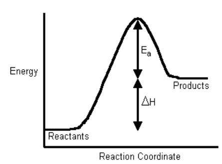


Enthalpy Change (ΔH)

Difference between the potential energies of the products and reactants



EXOTHERMIC



ENDOTHERMIC

Note which part is the ΔH!

Enthalpy Change (ΔH)

Difference between the potential energies of the products and reactants

- **EXAMPLE** (Stoichiometry)**:**

Upon adding potassium hydroxide pellets to water the following reaction takes place:

KOH(s) → KOH(aq) + 43 kJ/mol

When 14.0 g of KOH are added to water, what is the enthalpy change for the dissolution? Does the beaker get warmer or colder?

Heat of Formation (ΔH°_f)

- ΔH°_f for a pure element (including diatomics) is ZERO… you'll see in many AP problems that they just don't give you any values for pure elements so you must know this!
- If ΔH°_f is NEGATIVE, then energy is RELEASED when compound is formed and product is more STABLE than its elements
- If ΔH°_f is POSITIVE, then energy is ABSORBED when compound is formed and product is LESS stable than its elements

$\Delta H^\circ = \Sigma \Delta H^\circ_f$ PRODUCTS – $\Sigma \Delta H^\circ_f$ REACTANTS

Heat of Formation (ΔH°_f)

- **EXAMPLE** (Tables)**:**

Given the information below, calculate the ΔH°_{rxn} for the following reaction:

$3\ Al(s) + 3\ NH_4ClO_4(s) \rightarrow Al_2O_3(s) + AlCl_3(s) + 3\ NO(g) + 6\ H_2O(g)$

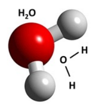
Substance	ΔH°_f (kJ/mol)
$NH_4ClO_4(s)$	-295
$Al_2O_3(s)$	-1676
$AlCl_3(s)$	-704
$NO(g)$	90.0
$H_2O(g)$	-242

Just like bond enthalpy… pay attention to the BALANCED equation!!

Bond Enthalpy

Energy required to break the bond between two covalently bonded atoms

(aka Bond Energy)



- Bonds BREAKING = Endothermic
- Bonds FORMING = Exothermic
- Takes energy to BREAK… Released when FORM
- Change in enthalpy (energy) for a reaction can be found using the bond energies:

ΔH_{rxn} = Σ(energies of bonds BROKEN) – Σ(energies of bonds FORMED)

Bond Enthalpy

Energy required to break the bond between two covalently bonded atoms

- **EXAMPLE (Bond Energy):**

Calculate the energy change that accompanies the following reaction given the data below:

$H_2(g) + F_2(g) \rightarrow 2\ HF(g)$

Bond	Bond Energy (kJ/mol)
H-H	432
F-F	154
H-F	565

Hess's Law

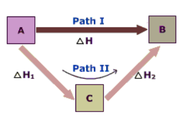
If a reaction can be described as a series of steps, then ΔH for the overall reaction is simply the sum of the ΔH values for all steps

THREE RULES:

1) Flip the equation… Flip the sign

2) Multiply or divide the equation by a #… Multiply or divide enthalpy value by same

3) When several equations are summed up to get a new equations… Add enthalpy values of the component equations



Hess's Law

If a reaction can be described as a series of steps, then ΔH for the overall reaction is simply the sum of the ΔH values for all steps

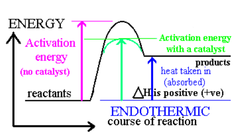
- **EXAMPLE (Hess's):**

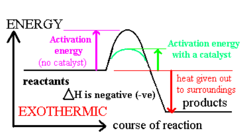
Calculate the ΔH for this overall reaction given the following:

$2\ H_3BO_3(aq) \rightarrow B_2O_3(s) + 3\ H_2O(l)$

$H_3BO_3(aq) \rightarrow HBO_2(aq) + H_2O(l)$	ΔH = -0.02 kJ/mol
$H_2B_4O_7(aq) + H_2O(l) \rightarrow 4\ HBO_2(aq)$	ΔH = -11.3 kJ/mol
$H_2B_4O_7(aq) \rightarrow 2\ B_2O_3(s) + H_2O(l)$	ΔH = 17.5 kJ/mol

Enthalpy Summary





- ΔH = "+"… Reaction is ENDOTHERMIC and heat energy is ADDED to the system
- ΔH = "-"… Reaction is EXOTHERMIC and heat energy is LOST from the system
- Nature tends to go towards the LOWEST energy state!

Practice

- **EXAMPLE:**

Calculate the standard change of enthalpy for the thermite reaction below using the information given:

$2\ Al(s) + Fe_2O_3(s) \rightarrow Al_2O_3(s) + 2\ Fe(s)$

Substance	$\Delta H°_f$ (kJ/mol)
$Fe_2O_3(s)$	-826
$Al_2O_3(s)$	-1676

Practice

- **EXAMPLE:**

Determine the ΔH_f of $C_6H_{12}O_6(s)$ given the reaction below and the following information:

$C_6H_{12}O_6(s) + 6\ O_2(g) \rightarrow 6\ CO_2(g) + 6\ H_2O(g) + 2800\ kJ$

Substance	ΔH°_f (kJ/mol)
$CO_2(g)$	-393.5
$H_2O(g)$	-285.8

Practice

- **EXAMPLE:**

Calculate the ΔH for the reaction below using the information given:

$2\ C(s) + H_2(g) \rightarrow C_2H_2(g)$

$C_2H_2(g) + 5/2\ O_2(g) \rightarrow 2\ CO_2(g) + H_2O(l)$ ΔH = -1299.6 kJ

$C(s) + O_2(g) \rightarrow CO_2(g)$ ΔH = -393.5 kJ

$H_2(g) + \frac{1}{2}\ O_2(g) \rightarrow H_2O(l)$ ΔH = -285.8 kJ

Heat Capacity (C_p)

Amount of heat needed to increase the temperature of an object by 1°C

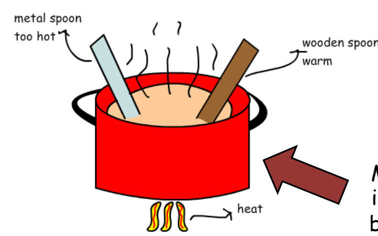
- **Extensive Property**... depends on how much! (Ex: ice cube vs. iceberg)

- SPECIFIC HEAT CAPACITY (C or C_p): amount of heat needed to raise 1 g of a substance by 1°C

-Water has a HIGH C_p (4.184 J/g°C)... need more heat to raise the temperature

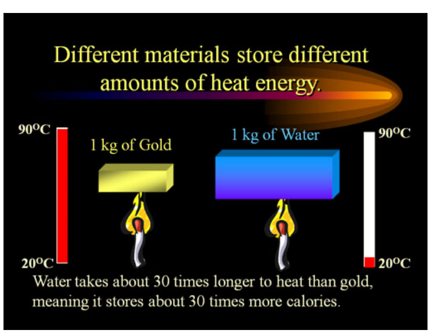
-Metals have a LOW C_p... less heat needed to raise the temperature

Specific Heat



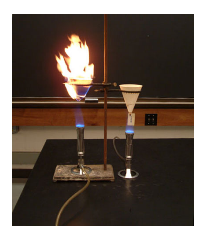
Metals are used in pots and pans because it takes little energy to heat them up!

Specific Heat



Specific Heat Problems

- Units are usually J/g°C or cal/g°C
- Equation: $q = mc\Delta T$



q = HEAT (Joules)

m = MASS (grams)

c = SPECIFIC HEAT

ΔT = FINAL Temp – INITIAL Temp (°C)

Specific Heat Problems

- **EXAMPLE:**

When 435 J of heat is added to 3.4 g of olive oil at 21°C, the temperature increases to 85°C. What is the specific heat of the olive oil?

$q = m\,c\,\Delta T$

$435\ J = (3.4\ g)\ c\ (85°C - 21°C)$

$c = 2.0\ J/g°C$

Practice

- **EXAMPLE:**

How many calories does 32.0 g of water absorb when it is heated from 25.0°C to 80.0°C?

Calorimetry

Process of measuring heat based on observing the temperature change when a body absorbs or discharges energy as heat

- CALORIMETER: device used to measure heat (ex: foam cup… good insulators)

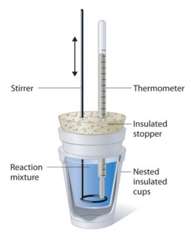
"Coffee Cup" Calorimetry

aka Constant Pressure Calorimetry

$q = \Delta H$

At these conditions…

We assume NO heat is lost to the surroundings

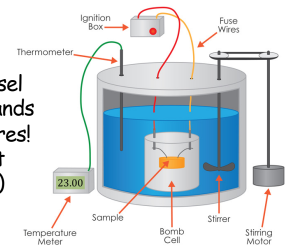


Calorimetry

Process of measuring heat based on observing the temperature change when a body absorbs or discharges energy as heat

Bomb Calorimeter

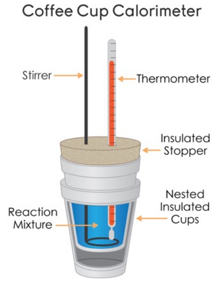
Sealed vessel that withstands high pressures! (Constant pressure)



Calorimetry

Process of measuring heat based on observing the temperature change when a body absorbs or discharges energy as heat

Coffee Cup Calorimeter



Calorimetry

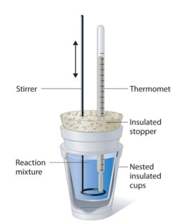
Process of measuring heat based on observing the temperature change when a body absorbs or discharges energy as heat

$+q_{sys} = -q_{surr}$

Heat gained by system will be SAME as heat lost by surroundings (and vice versa)!

HEAT LOST by substance = HEAT GAINED by water!

Conservation of Energy!!



Practice

- **EXAMPLE:**

An unknown metal with a mass of 75.8 grams is heated to a temperature of 80.0°C. It is then placed in 79.4 grams of water that is at a temperature of 18.5°C. The temperature of the water and metal then rise to a temperature of 23.5°C. What is the specific heat of the metal?

Calorimetry

Process of measuring heat based on observing the temperature change when a body absorbs or discharges energy as heat

- Can also use this to find the enthalpy of a reaction

***NOTE: There are SO MANY variations of these problems… the wording is key… you will need to be "on your toes" and THINKING!!**

Calorimetry

Process of measuring heat based on observing the temperature change when a body absorbs or discharges energy as heat

- **GENERAL STEPS:**

1) Use q= mcΔT… if mass not given, density can be used (assume density of water) to determine TOTAL mass of solutions being mixed and usually assume specific heat of the solution is 4.184 J/g °C

2) Solve for q… remember this is the heat of the resulting solution so the heat due to the reaction is OPPOSITE sign

3) Determine moles of substance formed (might need to do limiting problem if asking about product)

4) q / mol gives ΔH_{rxn} (kJ/mol_{rxn})

Calorimetry

Process of measuring heat based on observing the temperature change when a body absorbs or discharges energy as heat

- **EXAMPLE:**

In a calorimeter, 100.0 mL of 1.0 M NaOH and 100.0 mL of 1.0 M HCl are mixed. Both solutions were originally at 24.6°C. After the reaction, the final temperature is 31.3°C. Assume all solutions have a density of 1.0 g/cm^3 and a specific heat of 4.184 J/g °C. Calculate the energy change (kJ) for the reaction.

Practice

- **EXAMPLE:**

An experiment was conducted in which 5.19 g of Na_2CO_3 was dissolved in 75.0 g of distilled water. A temperature increase of the system of 3.80°C was observed. Find the molar enthalpy of dissolution of Na_2CO_3.

***TAKE NOTE…**

If the solid is just DISSOLVING (heat of solution / dissolution), then ADD the water and solid mass together for the total mass in the specific heat equation!!

Practice

- **EXAMPLE:**

An experiment was conducted in which 5.19 g of Na_2CO_3 was dissolved in 75.0 g of distilled water. A temperature increase of the system of 3.80°C was observed. Find the molar enthalpy of dissolution of Na_2CO_3.

***TAKE NOTE…**

If the solid is being BURNED / COMBUSTED / REACTED, then just use the mass of the water ONLY for the total mass in the specific heat equation!!

Practice

- **EXAMPLE:**

An experiment was conducted in which 5.19 g of Na_2CO_3 was dissolved in 75.0 g of distilled water. A temperature increase of the system of 3.80°C was observed. Find the molar enthalpy of dissolution of Na_2CO_3.

Practice

- **EXAMPLE:**

When 1.00 L of 2.00 M $Ba(NO_3)_2$ at 25°C is mixed with 1.00 L of 0.5 M Na_2SO_4 at 25°C in a calorimeter, the white solid $BaSO_4$ forms and the temperature of the mixture increases to 28.1°C. Assuming the specific heat is 4.184 J/g °C and that the density of the final solution is 1.0 g/mL, calculate the enthalpy change per mole of $BaSO_4$ formed.

Practice

- **EXAMPLE:**

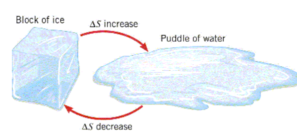
Gallium, a metal often used to make computer chips, can be purified by melting. Using the information given below, how much energy in kJ is required to melt 2.0 moles of gallium originally at 293 K?

Molar heat capacity of solid	$25.86\ J\ mol^{-1}K^{-1}$
Heat of fusion	$5.59\ kJ\ mol^{-1}$
Heat of vaporization	$256\ kJ\ mol^{-1}$
Melting point	$303\ K$

Second Law of Thermodynamics

UNIVERSE IS CONSTANTLY INCREASING THE DISPERSAL (DISORDER) OF MATTER AND ENERGY

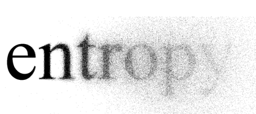
2nd Law of Thermo: Entropy



Entropy (S)

Measure of the randomness or disorder of the system

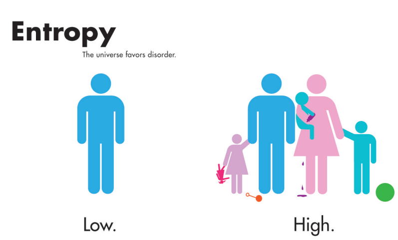
- GREATER the disorder, GREATER the entropy
- Zero entropy is a solid crystal at 0 K (no disorder at all)
- Never reached 0 K so all substances have a positive value for entropy, but overall processes can be negative!



DISORDER is preferred / favored... NATURE TENDS TOWARD CHAOS!!

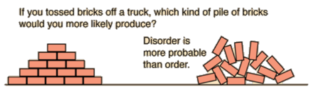
Entropy (S)

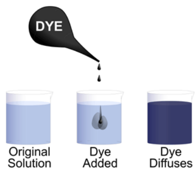
Measure of the randomness or disorder of the system



Entropy (S)

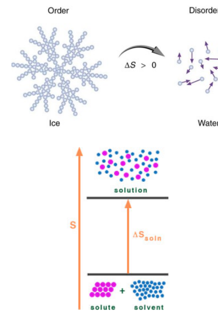
Measure of the randomness or disorder of the system





Entropy (S)

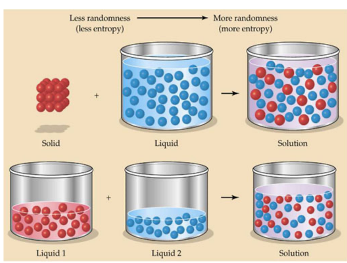
Measure of the randomness or disorder of the system



- Liquids = Higher entropy values than solids
- Gases = Higher entropy values than liquids
- Particles in solution = Higher entropy than solids
- Two moles of gas = Higher entropy than one mole of gas

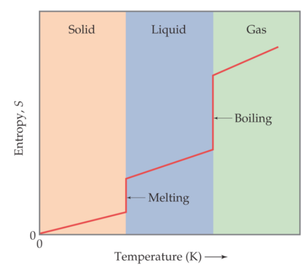
Entropy (S)

Measure of the randomness or disorder of the system



Entropy (S)

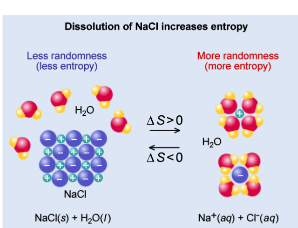
Measure of the randomness or disorder of the system

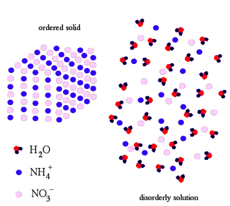


As temperature increases, S increases!

Entropy (S)

Measure of the randomness or disorder of the system





Entropy (S)

Measure of the randomness or disorder of the system

- To calculate standard entropy change for a reaction:

$$\Delta S^\circ = \Sigma S^\circ \text{ PRODUCTS} - \Sigma S^\circ \text{ REACTANTS}$$

- Units usually J/mol · K
- Pay attention to the balanced equation
- "+" ΔS = disorder increases (FAVORED)
- ΔS = 0 at equilibrium!

Entropy (S)

Measure of the randomness or disorder of the system

- **EXAMPLE:**

Calculate the entropy change at 25°C for the reaction below using the given data:

$2\ SO_2(g) + O_2(g) \rightarrow 2\ SO_3(g)$

Substance	S° (J/mol·K)
$SO_2(g)$	248.1
$O_2(g)$	205.3
$SO_3(g)$	256.5

Practice

- **EXAMPLE:**

Calculate the entropy change for the reaction below using the given data:

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

Substance	S° (J/mol·K)
$N_2(g)$	191.5
$H_2(g)$	130.6
$NH_3(g)$	193.0

Thermodynamically Favored

Processes or reactions that involve both a DECREASE in internal energy ($\Delta H^\circ < 0$) and an INCREASE in entropy ($\Delta S^\circ > 0$) are…

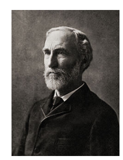
THERMODYNAMICALLY FAVORED!

*Note the terms spontaneous and nonspontaneous were used to describe favored and unfavored reactions previously… DO NOT USE THEM ON THE EXAM!!

Gibb's Free Energy (G)

Measure of whether or not a process will proceed without the input of outside energy

- ΔG ultimately determines whether a reaction is thermodynamically favorable or not
- "-" ΔG = Thermodynamically FAVORED
- "+" ΔG = Thermodynamically UNFAVORED
- ΔG = 0… At EQUILIBRIUM



Gibb's Free Energy (G)

Measure of whether or not a process will proceed without the input of outside energy

- To calculate standard free energy change for a rxn:

$$\Delta G^\circ = \Sigma\ \Delta G^\circ_f\ \text{PRODUCTS} - \Sigma\ \Delta G^\circ_f\ \text{REACTANTS}$$

- Units usually kJ/mol
- Pay attention to the balanced equation
- ΔG°_f = 0 for pure elements

Gibb's Free Energy (G)

Measure of whether or not a process will proceed without the input of outside energy

- **EXAMPLE:**

Calculate the free energy change for the following reaction using the data given:

$2\ H_2O(l) + O_2(g) \rightarrow 2\ H_2O_2(l)$

Substance	ΔG° (kJ/mol)
$H_2O(l)$	-237.1
$H_2O_2(l)$	-120.4

Gibb's Free Energy (G)

Measure of whether or not a process will proceed without the input of outside energy

- Nature moves towards two states… LOW energy and HIGH disorder
- How to determine favorability of a process relating free energy (G), enthalpy (H), and entropy (S):

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

- T = absolute temperature (K)
- Convert TΔS term to kJ/mol

Gibb's Free Energy (G)

Measure of whether or not a process will proceed without the input of outside energy

- Nature moves towards two states… LOW energy and HIGH disorder
- How to determine favorability of a process relating free energy (G), enthalpy (H), and entropy (S):

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

- R = 8.3145 J/mol·K
- K = equilibrium constant

Sign of ΔG can be used to predict whether K is > or < than 1… How?

Gibb's Free Energy (G)

Measure of whether or not a process will proceed without the input of outside energy

- Nature moves towards two states… LOW energy and HIGH disorder
- How to determine favorability of a process relating free energy (G), enthalpy (H), and entropy (S):

Sign of ΔG can be used to predict whether K is > or < than 1… How?

- Forward Favored = -ΔG and K > 1
- Reverse Favored = +ΔG and K < 1

Gibb's Free Energy (G)

Measure of whether or not a process will proceed without the input of outside energy

- **EXAMPLE:**

Calculate ΔH°, ΔS°, ΔG°, and K_{eq} at 25°C using the following data:

$$2\ SO_2(g) + O_2(g) \rightarrow 2\ SO_3(g)$$

Substance	ΔH°_f (kJ/mol)	S° (J/mol·K)
$SO_2(g)$	-297	248
$SO_3(g)$	-396	257
$O_2(g)$	0	205

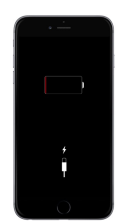
Favorability

ΔH	ΔS	T	ΔG	
–	+	Low	–	ALWAYS Favored
–	+	High	–	ALWAYS Favored
+	–	Low	+	NEVER Favored
+	–	High	+	NEVER Favored
+	+	Low	+	Not Favored at Low
+	+	High	–	Favored at High
–	–	Low	–	Favored at Low
–	–	High	+	Not Favored at High

At LOW temp ΔH wins… At HIGH temp ΔS wins!

Misconceptions

- If ΔG > 0, the process cannot occur… NOT TRUE! External sources of energy can be used to drive change (Ex: Electric current applied to charge a dead battery)



- If ΔG is large and negative, the process must proceed at a measureable rate… NOT TRUE! Kinetics related to HIGH ACTIVATION ENERGIES are important and play a role (Ex: held together by strong bonds or IMFs, collision orientation, E_a)