Unit#6
AP Chem
Topic #5
Thermo

Formula Page

Thermochemistry

$$\Delta E = q + w \quad w = -P\Delta V$$

$\Delta H = q_p$ (under constant pressure)

$q_{system} = -q_{surroundings}$

Constant Pressure Calorimetry(Coffee cup)

$q = s \times m \times \Delta T$
- q is heat (J) ($-q$ is exo and $+q$ is endo)
- s is the specific heat of the substance
- $\Delta T = T_f - T_i$

Constant Volume Calorimetry (bomb)

$q = C \times \Delta T$
- q is heat (J); $-q$ is exo and $+q$ is endo
- C is the specific heat of the bomb calorimeter (J/°C)
- $\Delta T = T_f - T_i$

Hess's Law

$$\Delta H_{rxn} = \Delta H_1 + \Delta H_2 + etc$$

Enthalpy of reaction (ΔH^o_{rxn})

$$\Delta H^o_{rxn} = \sum \Delta H^o_f(products) - \sum \Delta H^o_f(reactants)$$

The Nature of Energy

Potential Energy - energy by virtue of position. In chemistry, energy stored in bonds (bond energy, kJ/mol).
Energy is needed to BREAK bonds due to the coulombic attraction between electrons involved in the bond and the nuclei of the atoms.
- Coulombic force - force exerted by charged particles with regard to distance,
- Bonded atoms have a lowered PE (diagram)
- Energy is released when bonds FORM.

q_1 $\qquad F_e = \dfrac{kq_1q_2}{r^2}$ $\qquad q_2$

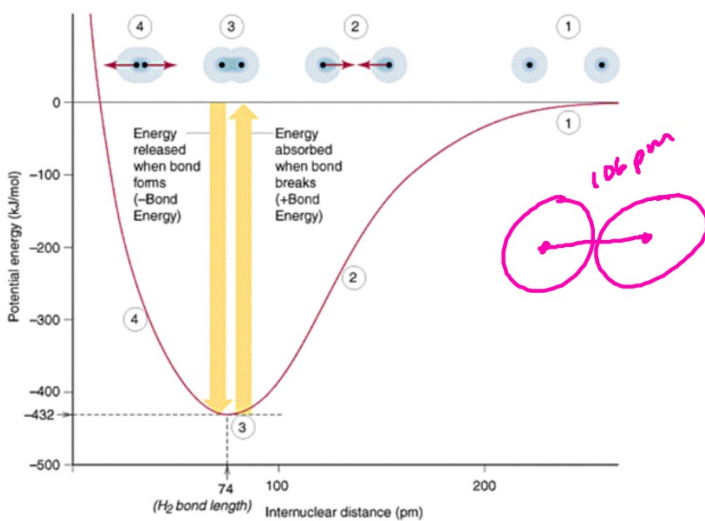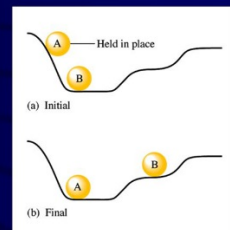$\longleftarrow - - - - r - - - - \longrightarrow$

Figure 6.1: (a) In the initial positions, ball A has a higher potential energy than ball B. (b) After A has rolled down the hill, the potential energy lost by A has been converted to random motions of the components of the hill (frictional heating) and to the increase in the potential energy of B.

The Nature of Energy

Kinetic Energy
- energy of motion, directly related to the temperature of sample ($KE = 1/2mv^2$).
- the KE of each species in a sample is equal at the same T.
- Boltzmann distribution curve
  - Activation energy (E_a) - the minimum energy needed to start a reaction

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$$A + B \rightarrow C$$
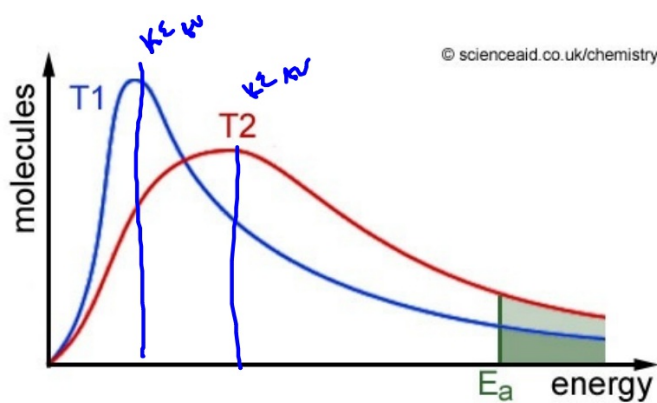
The Nature of Energy

Thermochemistry

- study of energy transformations (thermal (heat) transfers)
  - physics - the ability to do work (force applied over a distance)
  - chemistry - two forms, KE (energy of motion, kinetic E) and PE (stored energy, potential E)

Heat (q) - transfer of energy between two objects at two different temperatures.
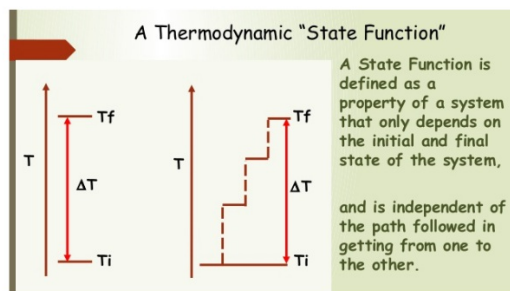
Temperature (T) - measurement used to determine heat transfer, proportional to KE_{av}
- "heat em up" to "speed them up"

Work (w) - a force acting over a distance ($w = F$ x d)

Law of Conservation of Energy - energy must be conserved, energy is never created or destroyed just converted to different forms. (AKA: **The First Law of Thermodynamics**)

State Function - a property of a system that depends only on its *present state*. (regardless of pathway)


A Thermodynamic "State Function"

A State Function is defined as a property of a system that only depends on the initial and final state of the system,

and is independent of the path followed in getting from one to the other.

The Nature of Energy

Chemical Energy

- Define system and surroundings
  - system - where primary activity is found
    - area of universe undergoing a physical/chemical change
  - surroundings - everything outside of system
- Endothermic - E flows into system (absorbs energy, $+\Delta E$)
- Exothermic - E flows out of system (release energy, $-\Delta E$)
- Internal energy of a system is the sum of the PE and KE of all the particles in the system.
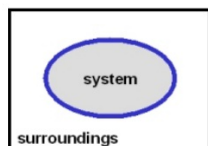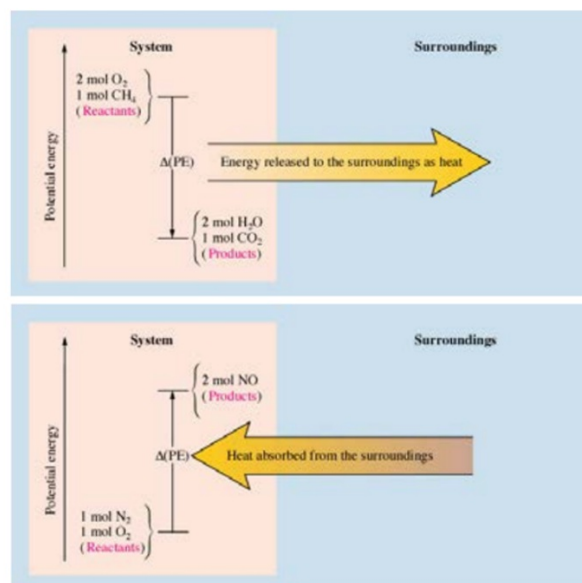

"Isolated" system:
· no exchange of matter
· no exchange of heat
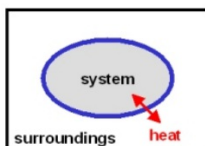
"Closed" system:
· no exchange of matter
· can exchange heat energy
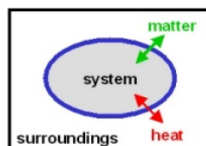
"Open" system:
· can exchange matter
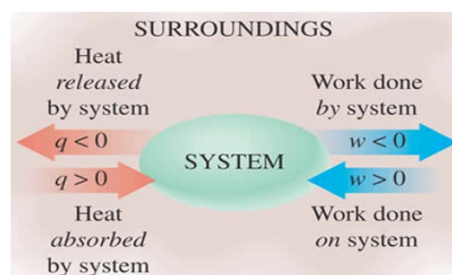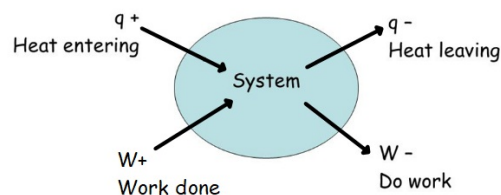· can exchange heat energy

The Nature of Energy

- Energy is the ability to do work.
  - $\Delta E = q$ (heat) $+ w$ (work)
    - the sign of q depends on whether energy is flowing in (+, endo) or out (-, exo) of the system.
      - $+q$ heat enters system
      - $-q$ heat leaves system
    - the sign of w depends on whether the system is doing work (-) or work is being done to the system (+).
      - $+w$ work done ON system by surroundings (compression)
      - $-w$ work done BY system (expansion)
- *Work* = $-P\Delta V$ (no change in volume, no work)

System vs Surroundings

Another way to solve for ΔE

$\Delta E = q + w = $ heat + work.   Sign direction issues!

q +
Heat entering

q –
Heat leaving

System

W+
Work done

W –
Do work

SURROUNDINGS

Heat *released* by system

$q < 0$

Work done *by* system

$w < 0$

SYSTEM

$q > 0$

$w > 0$

Heat *absorbed* by system

Work done *on* system

The Nature of Energy

Sample WS#1: Internal Energy

1. Calculate the ΔE for a system undergoing an endothermic process in which 15.6kJ of heat flows and where 1.4kJ of work is done on the system. (Ans: 17.0kJ)

Gun
$q = +15.6 \text{ kJ}$
$w = +1.4 \text{ kJ}$

NTK
$\Delta E = q + w$

Solve:
$\Delta E = 15.6 + 1.4 = \boxed{17.0 \text{ kJ}}$

Unk
$\Delta E = \underline{\qquad} \text{ kJ}$

2. Calculate the work associated with the expansion of a gas from 46L to 64L at a constant pressure of 15atm. (Ans: -270 L-atm)

Gun
$V_i = 46 \text{ L}$
$V_f = 64 \text{ L}$
$P = 15 \text{ atm}$

NTK
$w = -P\Delta V$
$\Delta V = V_f - V_i = 64 - 46 = 18 \text{ L}$

Solve:
$w = -(15)(18) = \boxed{-270 \text{ L} \cdot \text{atm}}$
   (atm) (L)

Unk
$w = \underline{\qquad} \text{ L} \cdot \text{atm}$

$101.3 \, kPa = 1 \, atm$

3. A balloon is being inflated to its full extent by heating the air inside it. In the final stages of this process, the volume of the balloon changes from 4.00×10^6 L to 4.50×10^6 L by addition of 1.3×10^8 J of energy as heat. Assuming that the balloon expands against constant pressure 1.0atm, calculate ΔE for the process. (To convert between L-atm and J, use 1L-atm = 101.3J).   Ans: 8.0×10^7J

Gvn

$V_i = 4.00 \times 10^6 \, L$

$V_f = 4.50 \times 10^6 \, L$

$q = +1.3 \times 10^8 \, J$

$P = 1 \, atm$

NTK

$\Delta E = q + w$

$w = -P \Delta V$

Unk

$\Delta E = \underline{\hspace{2cm}} \, J$

Solve: $w = -(1)(\overset{V_f}{4.50 \times 10^6} - \overset{V_i}{4.00 \times 10^6}) =$

$w = -5.00 \times 10^5 \, L \cdot atm \left(\dfrac{101.3 \, J}{L \cdot atm} \right)$

$w = \boxed{-5.1 \times 10^7 \, J}$

$\Delta E = (+1.3 \times 10^8 \, J) + (-5.1 \times 10^7 \, J)$

$= 8.0 \times 10^7 \, J$

$\boxed{8.0 \times 10^4 \, kJ}$

Enthalpy and Calorimetry

- **Enthalpy (H)** - flow of energy (heat exchange) at constant P between 2 items. Measured in kJ/mol$_{rxn}$.
    - measure only the change in enthalpy, ΔH.
    - state function
    - $\Delta H = q_p$ or $\Delta H = q_{rxn}$
        - q is measuered in joules while ΔH is measured in kJ (convert J to kJ by adding (x 10^{-3}) to its value)
            - 5409J becomes 5409x10^{-3} kJ (5.409 kJ)
- ΔH can be calculated from different sources
    - stoichiometry
    - calorimetry
    - from tables of standard values
    - Hess's Law
    - bond energies

Coffee Cup Calorimetry

$$q_p = s \times m \times \Delta T$$

$$\Delta H = \frac{kJ}{mol} = \frac{q \text{ (kJ)}}{moles_{prod}}$$

- $q_p = s \times m \times \Delta T$
  - q is the amount of heat moved
    - $-q$ moved from system to surroundings (exo)
    - $+q$ moved from surroundings to system (endo)
  - s (specific heat; can use the variable, C)
  - m is the mass of the system (when dissolving compounds, m, is the total mass of the water and compound)
  - ΔT is the change in temperature of the system with $\Delta T = T_f - T_i$
  - $q_{object} = -q_{water}$ (when an object is is immersed in water and a heat transfer starts)
    - After equilibrium has been reached, what is the temperature of both the object and water?

Specific Heats Capacities of
Some Common Substances

Substance	Specific Heat Capacity (J/°C-g)
$H_2O(l)$	4.18
$H_2O(s)$	2.03
$Al(s)$	0.89
$Fe(s)$	0.45
$Hg(l)$	0.14
$C(s)$	0.71

100 J Fe

100 g Al

Enthalpy/Calorimetry (Stoichiometrically)

4. Upon adding solid potassium hydroxide pellets to water the following reaction takes
   place: $KOH(s) \rightarrow KOH(aq) + 43kJ/mol$
   (a) Does the beaker become warmer or colder?
   (b) Is the reaction endothemic/exothermic?
   (c) What is the enthalpy change for the dissolution for 14.0g of KOH? (Ans: -10.7kJ)
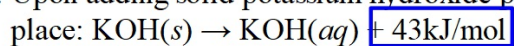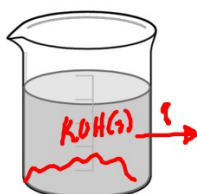
GVN

$\Delta H = -43 \text{ KJ/mol}$

$1 : 1$

$1 \text{ mol } KOH = -43 \text{ KJ}$

$14.0 \text{ g } KOH$

NTK

$1 \text{ mol } KOH = -43 \text{ KJ}$

$MM_{KOH} = 56.11 \text{ g/mol}$

Solve:

$$\frac{14.0 \text{ g } KOH}{} \cdot \frac{1 \text{ mol}}{56.11 \text{ g}} \cdot \frac{-43 \text{ KJ}}{1 \text{ mol}} = -10.729 \text{ KJ}$$

UNK

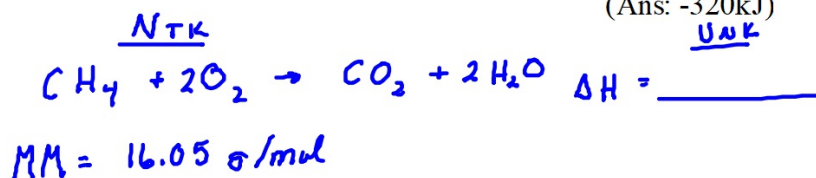$\Delta H = \underline{-11} \text{ KJ}$

$\boxed{-11 \text{ KJ}}$

KOH(s)

Enthalpy and Calorimetry

5. When 1 mole of methane (CH_4) is burned (combusted) at constant pressure (coffee cup), 890kJ of energy is released as heat. Calculate ΔH for a process in which a 5.8g sample of methane is burned (combusted) at constant pressure. (Ans: -320kJ)

<u>GvN</u>
1 mol CH_4 = -890 KJ
5.8g CH_4

<u>NTK</u>
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$
MM = 16.05 g/mol

<u>UNK</u>
$\Delta H = $ _____

SOLVE:

$$\frac{5.8g\ CH_4}{} \bigg| \frac{1\ mol}{16.05g} \bigg| \frac{-890\ KJ}{1\ mol} = 321.62\ KJ$$

$$\boxed{320\ KJ}$$

Enthalpy and Calorimetry

6. Consider the combustion of propane: $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$ (ΔH = -2221kJ). Assume that 1.3×10^8 J of energy comes from the combustion of propane. What mass of propane must be burned to furnish this amount of energy assuming the heat transfer process is 60.% efficient?   (Ans: 4400g)

<u>Gvn</u>
$\Delta H = 1.3 \times 10^8 J$
$(1.3 \times 10^5 KJ)$

<u>NTK</u>
60% efficient

$MM_{C_3H_8} = 44.11 g/mol$

<u>UnK</u>
$mass_{C_3H_8} = 4303g \; C_3H_8$

<u>Solve:</u>

$$\frac{1.3 \times 10^5 KJ}{0.60} \cdot \frac{*1}{-2221 KJ} \cdot \frac{1 mol \; C_3H_8}{-2221 KJ} \cdot \frac{44.11 g}{mol} = \boxed{4303 \; g \; C_3H_8}$$

*   If the process is 60% efficient, dividing by 0.60 will get you to 100% of original reactant/energy/etc.
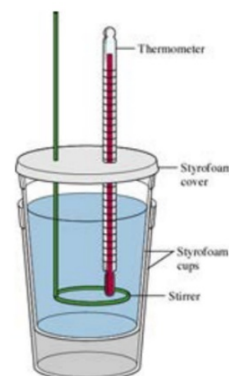
Calorimetry

$q_{syst} = -q_{surv}$

Calorimetry
- measuring heat by observing a temperature change when a body absorbs/loses energy as heat.
- coffee-cup calorimetry (@ constant *P)* - use nestled coffee cups to run an experiment where final temperature (T_f) and initial temperature (T_i), and mass/volume of reactants are collected.
  - ◆ $q = \Delta H$ (remember q is in J while ΔH is in kJ*)*
- Heat capacity - amount of energy needed to raise the *T* of 1gram of a substance by 1°C.
  - ◆ Specific heat capacity (C_p) - the heat capacity of a specific substance
    - S
    - ▪ water = 4.184 J/g-K, (note label)
    - ▪ 1cal = 4.184J
- Molar heat capacity - for 1 mole of substance (J/mol-K)
    - ▪ water = (18.02g/mol)(4.184J/g-K) = 75.40 J/mol-K
- Energy (q) released/gained (constant-pressure calorimetry)
    - ▪ $q = $ m x C_p x ΔT or m x S x ΔT
      - m is mass of substance
      - C_p or S is specific heat capacity of substance
      - $\Delta T = T_f - T_i$
    - ▪ $q_{rxn} = - q_{H2O}$ (heat either flows from water or is absorbed by water)

Thermometer

Styrofoam cover

Styrofoam cups

Stirrer

Calorimetry
Constant-Pressure Calorimetry

7. In a coffee cup calorimeter, 100.0mL of 1.0M NaOH and 100.0mL of 1.0M HCl are mixed. Both solutions were originally at 24.6°C. After reaction, the final temperature is 31.3°C. Assuming that all solutions have a density 1.0g/cm³ and a specific heat of 4.184J/g-°C, calculate the enthalpy change for the neutralization of HCl by NaOH. Assume that no heat is lost to the surroundings or the calorimeter   (Ans: -56kJ/mol$_{rxn}$)
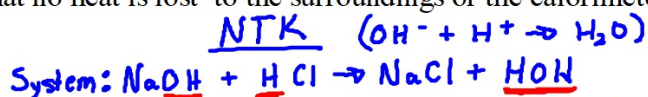
$\underline{Gvn}$

$T_i = 24.6°C$

$T_f = 31.3 °C$

$d_{soln} = 1.0 g/cm^3$

$S(C_p) = 4.184 J/g \cdot °C$

$\Delta H_{neut} = \dfrac{KJ}{mol_{rxn}}$

$\underline{NTK}$ $(OH^- + H^+ \to H_2O)$

System: $NaOH + HCl \to NaCl + HOH$

$\Delta T = T_f - T_i = 31.3 - 24.6 = \underline{6.7°C}$

$m_{HCl} = 100.0mL \times \dfrac{1g}{mL} = 100g$

$m_{NaOH} = 100.0mL \times \dfrac{1g}{mL} = 100g$

$q_{rxn} = -q_{surr(H_2O)}$

$\underline{UNK}$

$\Delta H_{neut} = \underline{-56 \frac{KJ}{mol_{rxn}}}$

$\bullet \Delta T$ of water
(q surr)
solvent (water)
is surroundings

$\underline{Solve:}$ $q_{H_2O} = m \times S \times \Delta T$

$= (200g)(4.184 \dfrac{J}{g \cdot °C})(6.7°C) = 5607 J$

$q_{rxn} = -q_{H_2O} = -(5607J)$

$\dfrac{100mL\,HCl}{} \left| \dfrac{1L}{1000mL} \right| \dfrac{1mol\,H^+}{1L} = 0.1 mol\,H_2O$

So, $\Delta H = \dfrac{KJ}{mol} = \dfrac{-5607J}{} \left| \dfrac{KJ}{1000\,J} \right| = -5.607kJ/0.1\,mol\,H_2O = \boxed{-56\dfrac{kJ}{mol_{rxn}}}$

Calorimetry

8. (OYO) When 1.00L of 1.0M Ba(NO$_3$)$_2$ solution at 25.0°C is mixed with 1.00L of 1.00M Na$_2$SO$_4$ solution 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 calorimeter absorbs only a negligible quantity of heat and that the specific heat capacity of the solution is 4.18J/°C-g, and the density of the final solution is 1.0g/mL, calculate the enthalpy change per mole of BaSO$_4$ formed. (Ans: -26kJ/mol$_{rxn}$)

Calorimetry

Constant-Volume Calorimetry
- reaction takes place in a bomb calorimeter
- $q = C_p \times \Delta T$

- where C_p is the heat capacity of the bomb calorimeter
- combustion of gases to determine heat of combustion, $\Delta H°_{comb}$

9. It has been suggested that hydrogen gas obtained by the decomposition of water might be a substitute for natural gas (principally methane). To compare the energies of combustion of these fuels, the following experiment was carried out using a bomb calorimeter with a heat capacity of 11.3kJ/°C. When a 1.50g sample of methane gas was burned with excess oxygen in the calorimeter, the temperature increased by 7.3°C. When a 1.15g sample of hydrogen gas was burned with excess oxygen, the temperature increase was 14.3°C. Compare the energies of combustion (per gram) for hydrogen and methane.

(Ans: 2.5 times more energy per gram of H than per gram of CH$_4$)

Gvn
$$S(C_p) = 11.3 \ KJ/°C$$
$$m_{CH_4} = 1.50g$$
$$\Delta T = 7.3°C$$
$$m_{H_2} = 1.15g$$
$$\Delta T = 14.3°C$$

NTK
$$q = C_p \times \Delta T$$

UnK

Solve:
$$H_2: \ q = C_p \times \Delta T = 11.3 \ KJ/°C \times 14.3°C = 161.59 \ KJ / 1.15g \ H_2$$
$$CH_4: \ q = C_p \times \Delta T = 11.3 \ KJ/°C \times 7.3°C = 82.49 \ KJ / 1.50g \ CH_4$$

$$1g \ H_2 \times \frac{161.59 KJ}{1.15g} = 140.5 \ KJ$$
$$1g \ CH_4 \times \frac{82.49 \ kJ}{1.50g} = 54.99 \ KJ$$

$$1g \ H_2 \ vs. \ 1g \ CH_4$$
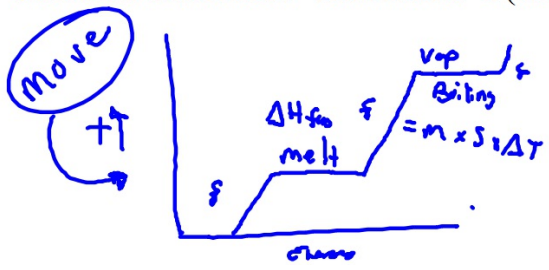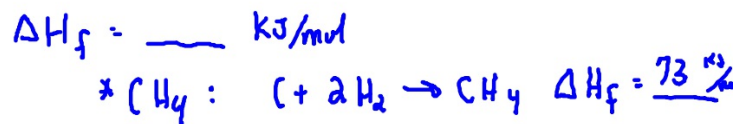$$\frac{140.5}{54.99} \quad \frac{54.99}{54.99}$$
$$\boxed{2.6 : 1}$$

Enthalpy Change

- **Enthalpy (ΔH)** - flow of energy (heat exchange) at constant P between 2 items. Measured in kJ/mol$_{rxn}$.
    - $+\Delta H$ is when heat enters a system, exits surroundings (endothermic, net absorption of energy by system)
    - $-\Delta H$ is when heat leaves a system, enters surroundings (exothermic, net release of energy by system)

$\Delta H > 0$

$\Delta H < 0$

  - ΔH_{rxn} is enthalpy of reaction.
  - ΔH_{comb} is enthalpy of combustion (burning), release oxides of combusted material
  - ΔH_f is enthalpy of formation of 1 mole of a compound from its constituent elements.
    Elements are in their standard states. ΔH_f for elements in their standard state is 0 kJ/mol
     - for $Na(s)$, $O_2(g)$, $Hg(l)$, etc the ΔH_f is ZERO
  - ΔH_{fus} is heat absorbed to melt 1 mol of a solid @ mp (energy needed to overcome IMF's, IMF's are
    forces that hold particles together to form liquids and solids) .
       - $\Delta H_{fus}(H_2O) = 6.009$kJ/mol   Calculate E = (moles)(ΔH) = KJ's
  - ΔH_{vap} is heat absorbed to vaporize 1 mole (overcome IMF's) of liquid @ bp.
       - $\Delta H_{vap}(H_2O) = 40.7$kJ/mol
- **Standard Conditions** - 1atm and 25°C (298K) ΔH_f = ___ kJ/mol

$* CH_4 :$ $C + 2H_2 \rightarrow CH_4$ $\Delta H_f = \underline{73 \frac{kJ}{mol}}$

move

$+\uparrow$

ΔH_{fus} & melt

vap Boiling

$= m \times S \times \Delta T$

s

s

s

change

Enthalpy Change

ENDOTHERMIC

Potential energy (kJ)

activated complex

products

activation energy E_a

reactants

$+ \Delta H$ $\Delta H > 0$

reaction pathway

EXOTHERMIC

Potential energy (kJ)

activated complex

activation energy E_a

reactants

$- \Delta H$ $\Delta H < 0$
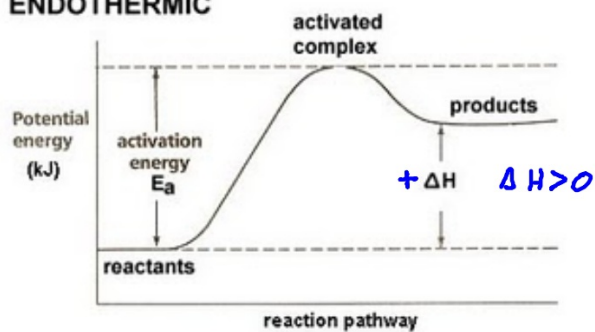
products

Exothermic   **Endothermic**

Heat

Heat — Hotter than surroundings — Heat

Heat

Heat

Heat — Cooler than surroundings — Heat

Heat

(?)
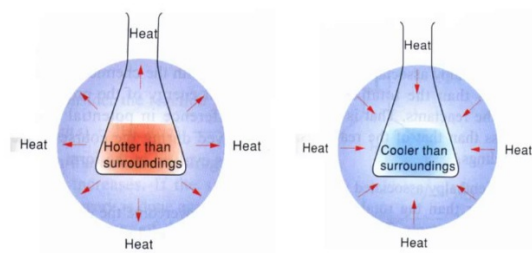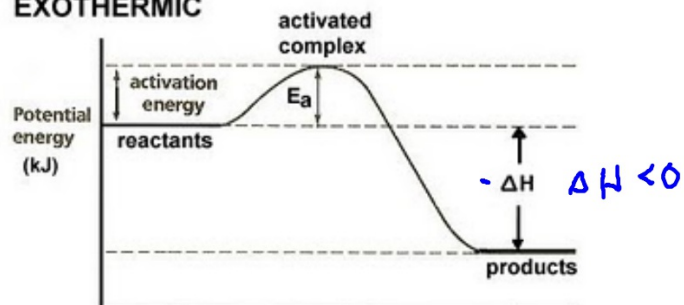
1 mol of a solid @ mp

move!!

Heats of Formation

> **Big Mamma Equation** $\Delta H_{rxn} = \sum \Delta H_{f(products)} - \sum \Delta H_{f(reactants)}$

ΔH_{rxn} can be calculated from the reaction's individual compounds' heat of formation.

Thermo Sample Problems WS#2 - Heats of Formation

1. Given the following information, calculate the ΔH°_{rxn} for the chemical reaction:

$3Al(s) + 3NH_4ClO_4(aq) \rightarrow Al_2O_3(s) + AlCl_3(aq) + 3NO(g) + 6H_2O(g)$
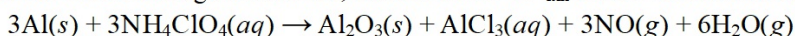
Substance	ΔH°_f(kJ/mol)
$NH_4ClO_4(aq)$	-295
$Al_2O_3(s)$	-1676
$AlCl_3(aq)$	-704
$NO(g)$	90.0
$H_2O(g)$	-242

(Ans: -2,677 kJ/mol$_{rxn}$)

Gvn
Data (ΔH)

NTK
$\Delta H_{rxn} = \sum \Delta H_{prod} - \sum \Delta H_{react}$

UnK

Solve: $\Delta H_{rxn} = [\Delta H_f (Al_2O_3) + \Delta H_f(AlCl_3) + 3\Delta H_f(NO) + 6\,\Delta H_f (H_2O)]$
$- [3\Delta H_f (Al) + 3\Delta H_f (NH_4ClO_4)]$
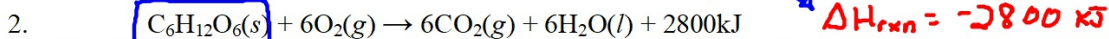
$\Delta H_{rxn} = ((-1676) + (-704) + 3(90) + 6(-242)) - (3(0) + 3(-295))$

$= (-3652) - (-885) = \boxed{-2677 \text{ KJ}}$

Heats of Formation

2. $C_6H_{12}O_6(s)$ + 6$O_2(g)$ → 6$CO_2(g)$ + 6$H_2O(l)$ + 2800kJ $\Delta H_{rxn} = -2800 \text{ kJ}$

Occasionally, not all values are found in the table of thermodynamic data. For most substances, it is impossible to go into a lab and directly synthesize a compound from its free elements. The heat of formation for the substance must be calculated by working backwards from its heat of combustion. Calculate the ΔH_f of $C_6H_{12}O_6(s)$ given the combustion reaction above along with the following information: (Ans: -1276 kJ/mol$_{rxn}$)

Substance	ΔH_f°(kJ/mol)
$CO_2(g)$	-393.5
$H_2O(l)$	-285.8

Gon
Data

NIK
$\Delta H_{rxn} = \sum \Delta H_{prod} - \sum \Delta H_{react}$

Unk
$\Delta H_f (C_6H_{12}O_6) = $ _____

Solve :

$-2800 = [6\Delta H_f(CO_2) + 6\Delta H_f(H_2O)] - [\Delta H_f(C_6H_{12}O_6) + 6\Delta H_f(O_2)]$

$-2800 = (6(-393.5) + 6(-285.8)) - (\Delta H_f(C_6H_{12}O_6) + 6(0))$

$-2800 = -2361 + (-1714.8) - \Delta H_f(C_6H_{12}O_6)$

$-2800 + 2361 + 1714.8 = -\Delta H_f(C_6H_{12}O_6)$

$1275.8 = -\Delta H_f(C_6H_{12}O_6)$

$\Delta H_f(C_6H_{12}O_6) = \boxed{-1275.8 \text{ kJ/mol}}$

Heats of Formation

3. The thermite reaction occurs when a mixture of powdered aluminum and iron (III) oxide is ignited with a magnesium fuse. Using enthalpies of formation, calculate the standard change in enthalpy for the thermite reaction.   (Ans: -850kJ)

<u>Gvn</u>   <u>NTK</u>   <u>UnK</u>

Data $2Al + Fe_2O_3 \rightarrow 2Fe + Al_2O_3$ $\Delta H_{rxn} = $ _____ KJ

$\Delta H_{rxn} = \sum \Delta H_{f\,(prod)} - \sum \Delta H_{f\,(react)}$
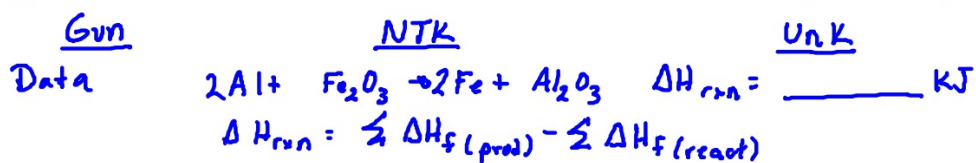
<u>Solve:</u> $\Delta H_{rxn} = \left(2\Delta H_f(Fe) + \Delta H_f(Al_2O_3)\right) - \left(2\Delta H_f(Al) + \Delta H_f(Fe_2O_3)\right)$

$= \Delta H_f(Al_2O_3) - \Delta H_f(Fe_2O_3)$

$= (-1676) - (-826) = \boxed{-850 \text{ KJ}}$

Table 6.2 Standard En thalpies of Formation Several Compounds a 25°C

Compound	ΔH_f° (kJ
$NH_3(g)$	-4
$NO_2(g)$	3
$H_2O(l)$	-28
$Al_2O_3(s)$	-167
$Fe_2O_3(s)$	-82
$CO_2(g)$	-39
$CH_3OH(l)$	-2
$C_8H_{18}(l)$	-20

Hess's Law

- Hess's Law
  - $\Delta H_{rxn} = \Delta H_1 + \Delta H_2 + \Delta H_3 +$ etc
  - Characteristics of ΔH for a Reaction
    - If a reaction is reversed, the sign on ΔH is also reversed
    - ΔH is directly propotionate to quantities involved in reaction, if the coefficients are multiplied by an integer, so is ΔH.

Hess's Law
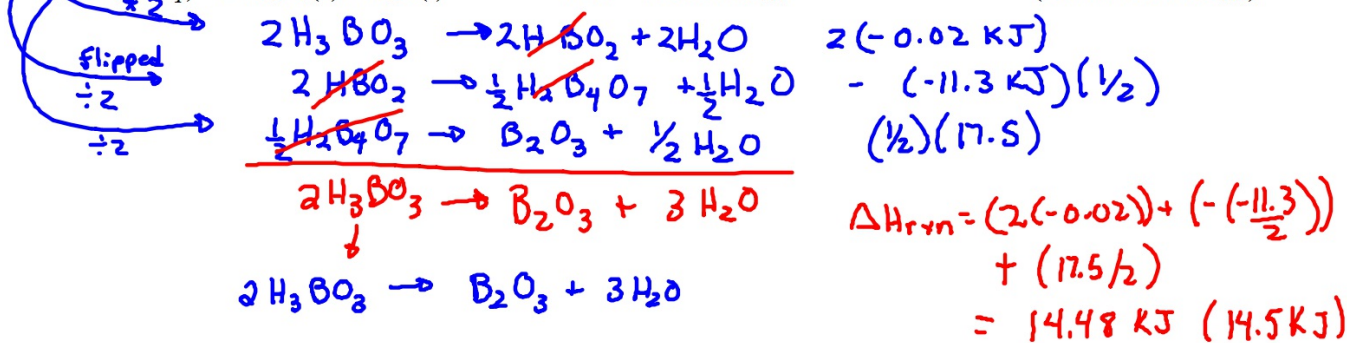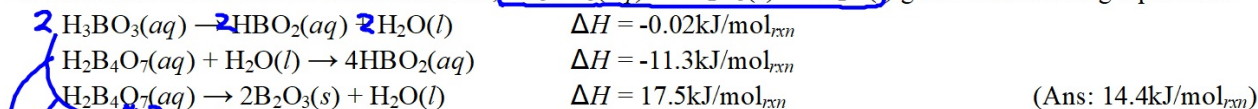
$$\Delta H_{rxn} = \Delta H_1 + \Delta H_2 + \text{etc}$$

Remember *enthalpy* is independent of pathway, so a combination of chemical reactions can be added up to give an overall reaction. A sum of the ΔH's from these reactions will be equal to the ΔH of the overall reaction.

Manipulations:

(1) Multiply/Divide by a whole number (multiply/divide ΔH by the same whole number)

(2) Reverse reaction (changes the sign on ΔH)

4. Calculate the ΔH for this overall reaction, $2H_3BO_3(aq) \rightarrow B_2O_3(s) + 3H_2O(l)$ given the following equations:

2 $H_3BO_3(aq) \rightarrow$ **2** $HBO_2(aq)$ **2** $H_2O(l)$ $\qquad \Delta H = -0.02kJ/mol_{rxn}$

$H_2B_4O_7(aq) + H_2O(l) \rightarrow 4HBO_2(aq)$ $\qquad \Delta H = -11.3kJ/mol_{rxn}$

$H_2B_4O_7(aq) \rightarrow 2B_2O_3(s) + H_2O(l)$ $\qquad \Delta H = 17.5kJ/mol_{rxn}$ $\qquad$ (Ans: 14.4kJ/mol$_{rxn}$)

*2

flipped
÷2

÷2

$2H_3BO_3 \rightarrow 2H BO_2 + 2H_2O$ $\qquad 2(-0.02\ KJ)$

$2HBO_2 \rightarrow \frac{1}{2}H_2B_4O_7 + \frac{1}{2}H_2O$ $\qquad -(-11.3\ KJ)(\frac{1}{2})$

$\frac{1}{2}H_2B_4O_7 \rightarrow B_2O_3 + \frac{1}{2}H_2O$ $\qquad (\frac{1}{2})(17.5)$

$2H_3BO_3 \rightarrow B_2O_3 + 3H_2O$

$2H_3BO_3 \rightarrow B_2O_3 + 3H_2O$

$\Delta H_{rxn} = (2(-0.02)) + (-(-\frac{11.3}{2}))$
$+ (17.5/2)$
$= 14.48\ KJ\ (14.5\ KJ)$

Bond Energies

$$\Delta H = \sum \text{Bond Energies}_{\text{Broken}} - \sum \text{Bond Energies}_{\text{Formed}}$$
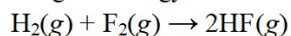
(reactant bonds)   (product bonds)

Remember:
   It takes ENERGY to BREAK bonds
   FORMED bonds RELEASE energ

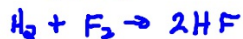5. Calculate the change in energy that accompanies the following reaction given the data below:

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

Bond Type	Bond Energy
H-H	432 kJ/mol
F-F	154 kJ/mol
H-F	565 kJ/mol

(Ans: -544kJ/mol$_{rxn}$)

Gvn
data

NTK
$H_2 + F_2 \rightarrow 2HF$
$\Delta H_{rxn} = \sum \text{Bonds broken} - \sum \text{Bonds formed}$

Solve: $H-H + F-F \rightarrow 2(H-F)$
$\Delta H_{rxn} = [(432) + (154)] - [2(565)]$
$= 586 - 1130 = \boxed{-544 \text{ KJ}}$

Unk
$\Delta H_{rxn} = \underline{-544 \text{ KJ}}$

Bond Energies

$$\Delta H = \sum \text{Bond Energies}_{\text{Broken}} - \sum \text{Bond Energies}_{\text{Formed}}$$
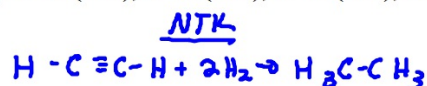(reactant bonds)   (product bonds)

Remember:
 It takes ENERGY to BREAK bonds
 FORMED bonds RELEASE energy

6. Hydrogenation of double and triple bonds is an important industrial process. Calculate (in kJ) the standard enthalpy change ΔH for the hydrogenation of ethyne (acetylene) $H-C\equiv C-H(g) + 2H_2(g) \rightarrow H_3C-CH_3(g)$
 Bond enthalpies (in kJ/mol): C−C (347); C≡C (839); C−H (413); H−H (432)   (Ans: -296kJ/mol$_{rxn}$)

Gvn
data

NTK
$H-C\equiv C-H + 2H_2 \rightarrow H_3C-CH_3$

Unk
$\Delta H_{rxn} = \underline{-296}$ KJ

Solve: $H \cdot C \equiv C-H + 2(H \cdot H) \rightarrow H-\overset{H}{\underset{H}{C}} - \overset{H}{\underset{H}{C}} - H$
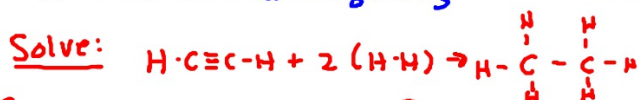
$\Delta H_{rxn} = [2(C-H) + (C\equiv C) + 2(H-H)] - [6(C-H) + (C-C)]$

$\Delta H_{rxn} = [2(413) + (839) + 2(432)] - [6(413) + (347)]$

$= (826 + 839 + 864) - (2825)$
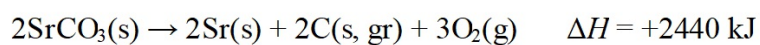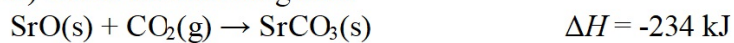
$= 2529 - (2825) = \boxed{-296 \text{ KJ}}$

_____ **Thermochemistry** _____
Topic#5

Hess's Law

$$\Delta H = \sum \Delta H_{f(\text{products})} - \sum \Delta H_{f(\text{reactants})}$$

7. (OYO) Given the following data:

$SrO(s) + CO_2(g) \rightarrow SrCO_3(s)$ $\Delta H = -234$ kJ

$2SrO(s) \rightarrow 2Sr(s) + O_2(g)$ $\Delta H = +1184$ kJ

$2SrCO_3(s) \rightarrow 2Sr(s) + 2C(s, gr) + 3O_2(g)$ $\Delta H = +2440$ kJ

Find the ΔH of the following reaction: $C(s, gr) + O_2(g) \rightarrow CO_2(g)$ (Ans: -394kJ/mol$_{rxn}$)

Bond Energies

$$\Delta H = \sum \text{Bond Energies}_{Broken} - \sum \text{Bond Energies}_{Formed}$$

8. (OYO) Using bond enthalpies, calculate the reaction enthalpy (ΔH) for:

$$CH_4(g) + Cl_2(g) \rightarrow CH_3Cl(g) + HCl(g).$$
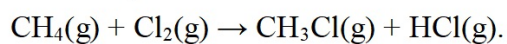
Bond enthalpies (in kJ/mol): C−H (413); Cl−Cl (239); C−Cl (339); H−Cl (427)   (Ans: -114kJ/mol$_{rxn}$)

Bond Energies

Speaking of bond energies, lets clear up some common misconceptions AND make some dazzling connections!

1) Vocabulary for phase changes is *directional* as well as very specific. You will have to mean what you say and say what you mean within a FRQ.

2) Phase transitions involve *overcoming* intermolecular forces (IMF) - London dispersion forces, hydrogen bonding, dipole-dipole forces, and ion-dipole forces.

3) Fusion (melting), vaporization, and sublimation require an input of energy to overcome the attractive forces (IMF) between particles of substance in a liquid or solid phase.

4) Freezing, condensation, and deposition release energy as IMFs form, since particles achieve a lower energy state (due to a decrease in temperature).

5) Difference between vapor and gas (semantics) - a gas is a gas at room T (don't say "oxygen vapor"). A vapor is the gaseous phase of a liquid at room temperature ("water vapor" is gaseous water molecules above liquid water at room T).

6) Be very, very clear that changes in phase only involve altering IMF, not altering chemical bonds (covalent, ionic).

   - strength of IMF depends on the characteristics of the substance (ionic, molecular (polar vs. nonpolar)

$$\Delta H_{fusion(H_2O)} = 6.009$$

$$\Delta H_{vap(H_2O)} = 40.7$$

Why is the $\Delta H_{vap(H_2O)}$ so much larger than the $\Delta H_{fus(H_2O)}$?

Bond Energies

7) Generally, the more polar a molecule is, the stronger the attractive forces between molecules.
8) More polar molecules require more *energy* to overcome these attractive forces in an *endothermic phase transition* (melting, vaporization, and sublimation) and release more *energy* during an *exothermic phase transition* (freezing, condensation, and deposition).
9) Phase transitions involve the "breaking" or "forming" of IMFs (attractive forces between particles).
10) It is necessary to discuss the energy transformations that occur with the breaking/forming of these forces.
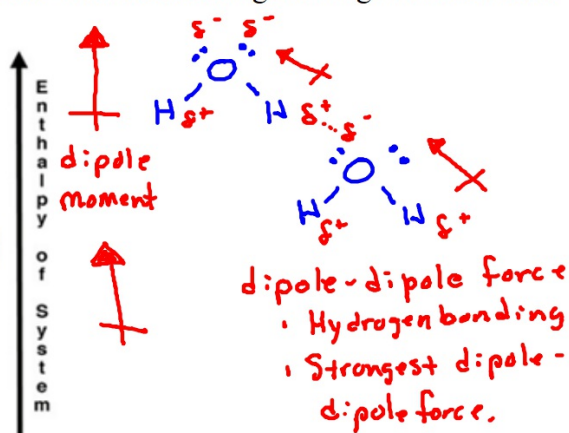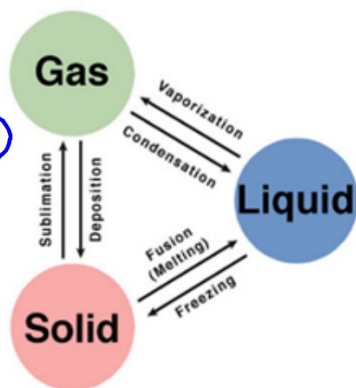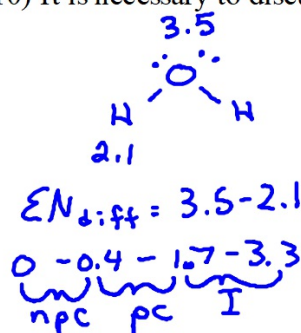
Heating Curve

1) Should the A/B line be longer or shorter than the C/D line for a heating curve of water? Why?

2) Does the process above represent a collection of chemical changes, physical changes or both?

3) What type of force is involved in the changes you identified in question 2?

intermolecular forces (IMF)   dipole-dipole (H-bonding)
LDF - London dispersion forces

4) Define temperature.

KE_{AV}

5) What parts of the curve involve temperature change?

heating/cooling of a phase

6) Which mathematical formula is appropriate for calculating the energy associated with the processes you identify in question 5?

$$q = m \times S \times \Delta T$$
(C_p)

7) Which conversions on the curve involve potential energy changes?

phase changes ($s \rightarrow l$, $l \rightarrow g$)

8) Which mathematical formula is appropiate for calculating the energy associated with the processes you identify in question 7?

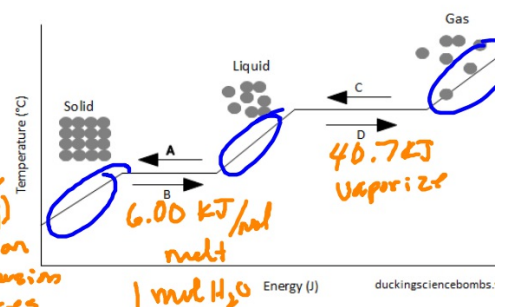(moles of substance) $\times \Delta H_{vap}$ or ΔH_{fus}

9) How do you calculate q for the processes identified in number 8 if you are only given the mass of the water sample?

Convert mass into moles then multiply by ΔH_{fus} or ΔH_{vap}
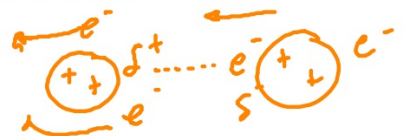
10) Which portions of the graph represent equilibrium conditions?   A & B   C & D

Gas
Liquid
Solid

40.7 kJ
vaporize

6.00 kJ/mol
melt

1 mol H_2O Energy (J)   duckingsciencebombs.

→ induced dipoles

Heating Curve

11) Calculate the amount of energy needed to heat a 55.5g sample of water from -15.0°C to 140.°C. (Ans: 172kJ)

① $\Delta T = 0 - (-15) = 15$
  $q = (55.5)(2.108)(15) =$ 1755 J ✱

② $\Delta H = 55.5 \times \dfrac{1\,mol}{18.02} \times \dfrac{6.02\,kJ}{mol} =$ 18.5 kJ

③ $\Delta T = 100 - 0 = 100$
  $q = (55.5)(4.18)(100) =$ 23,199 J ✱

④ $\Delta H = \left(55.5 \times \dfrac{1\,mol}{18.02}\right) \times \dfrac{40.7\,kJ}{mol} =$ 125.4 kJ

⑤ $\Delta T = 140 - 100 = 40$
  $q = (55.5)(1.996)(40) =$ 4431 J ✱

$q_{rxn} = 1 + 2 + 3 + 4 + 5$

$= \dfrac{1755}{1000} + 18.5 + \dfrac{23,199}{1000} + 125.4 + \dfrac{4431}{1000}$

$= \boxed{173\,kJ}$
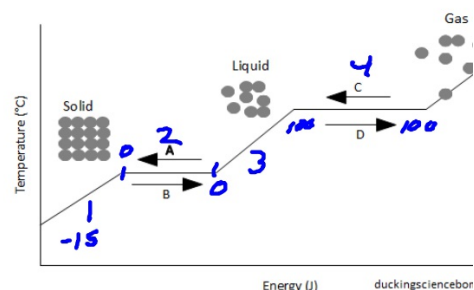
Substance
$S_{H2O(s)} = 2.108$ J/g-°C
$S_{H2O(l)} = 4.184$ J/g-°C
$S_{H2O(g)} = 1.996$ J/g-°C
$\Delta H_{fus} = 6.02$ kJ/mol
$\Delta H_{vap} = 40.7$ kJ/mol

Thermodynamics
Entropy (*S*) & Free Energy (*G*)

Thermodynamic Formulas

Entropy

$$\Delta S^{\circ}_{rxn} = \sum \Delta S^{\circ}_{products} - \sum \Delta S^{\circ}_{reactants}$$

$$\Delta S_{surroundings} = \frac{\text{heat transferred}}{\text{temperature at which change occurs}} = \frac{q}{T} = \frac{-\Delta H}{T} \text{ expressed in } \frac{J}{mol_{rxn} \cdot K}$$

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings}$$

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

Gibb's Free Energy

$$\Delta G^{\circ}_{rxn} = \sum \Delta G^{\circ}_{products} - \sum \Delta G^{\circ}_{reactants}$$

$$\Delta G^{\circ}_{rxn} = \Delta H^{\circ} - T\Delta S^{\circ}$$

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

$$K = e^{-\Delta G/(R \times T)} \text{ or } K = e^{-\Delta G/2.47}$$

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

$$\Delta G = -nFE^{\circ}$$

Thermodynamics

- **Entropy (ΔS)** - measure of the dispersal (disorder) of matter and energy, measured in J/K.
    - $+\Delta S$ increase in dispersal (disorder) $\Delta S > 0$
    - $-\Delta S$ decrease in dispersal (disorder) $\Delta S < 0$
- **Gibb's Free Energy (ΔG)** - determines themodynamic favorability and calculating the theoretical amount of energy to do work. Measured in kJ/mol$_{rxn}$.
    - $+\Delta G$ indicates non-spontaneous reaction (not thermodynamically favorable reaction) $\Delta G > 0$
    - $-\Delta G$ indicates spontaneous reaction (thermodynamically favorable reaction) $\Delta G < 0$
- **Thermodynamics** - study of energy and its interconversions.
- **Work** - Force acting over a distance, $w = F \times d = -P\Delta V$ (where gases are involved)

(Amend)

Thermodynamics

What drives a reaction to be thermodynamically favorable?
- ΔH : enthalpy, amount of heat exhange (exothermic (-ΔH) processes are favorable)
- ΔS : entropy, amount of dispersal (disorder) in a system (an increase (+ΔS) in dispersal (disorder) is favorable).
- Thermodynamically favored reactions involve both a decrease in system energy ($\Delta H<0$)and an increase in entropy ($\Delta S>0$).
- Remember from electrochemistry, a ΔG less than zero is a thermodynamically favored reaction.
     * Do not use "spontaneous" to describe a thermodynamically favored reaction.
        Use "**thermodynamically favored**."
- Thermodynamics does not predict nor take into account the rate of reaction (kinetics, next topic).
- Some reactions are fast (combustion of hydrogen) or slow (graphite to diamonds) but both are thermodynamically favored.
- 1st Law of Thermodynamics - energy is conserved.
- 2nd Law of Thermodynamics - the universe is constantly increasing the dispersal of matter and energy ($\Delta S_{univ} > 0$).
- 3rd Law of Thermodynamics - the entropy of a perfect crystal at 0K is zero. Not many perfect crystals so the absolute entropy for any substance can be determined for any $T > 0$K. (Handy if you need to defend why G and H for elements is zero, but S is not!

Entropy (*S*)

Ideal gas expansion.
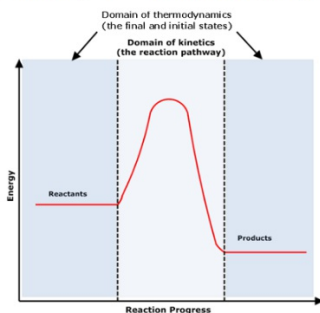
- What is entropy anyway? - thermodynamic function that describes the *number of arrangements* (positions and/or energy
  levels) that are available to a system existing in a given state. Nature spontaneously proceeds toward the states that have the highest probabilities of existing.

Why is this process thermodynamically favorable?

More ways of having the gas evenly disperse than for it to be in any other state.
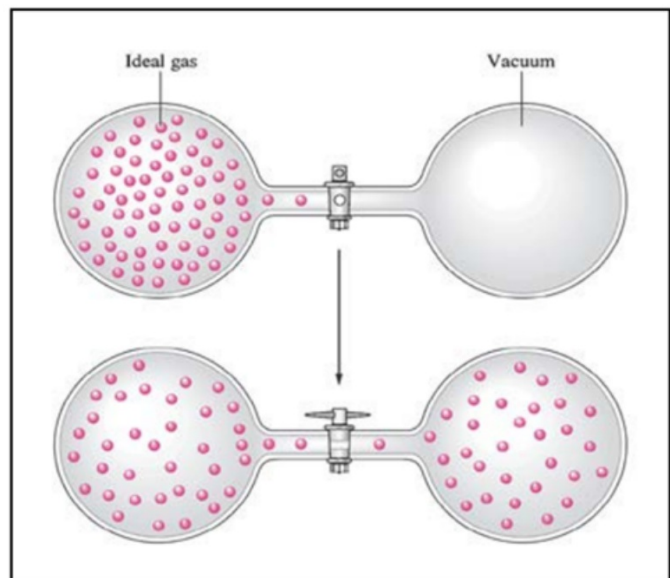
Entropy (S)
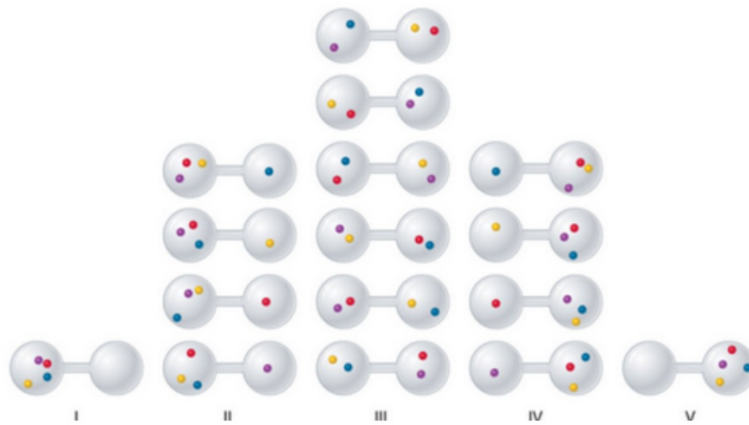
There are 16 different ways to distribute four gas molecules between the bulbs, with each distribution corresponding to a particular microstate. Arrangements I and V each produce a single microstate with a probability of 1/16. This particular arrangement is so improbable that it is likely not observed. Arrangements II and IV each produce four microstates, with a probability of 4/16. Arrangement III, with half the gas molecules in each bulb, has a probability of 6/16. It is the one encompassing the most microstates, so it is the most probable.

Entropy (S)

Predicting the entropy of a system is based on physical evidence:

- The greater the dispersal of matter and/or energy in a system, the larger the entropy.
- The entropy of a substance always increases as it changes from solid to liquid to gas.
- When a pure solid or liquid dissolves in a solvent, the entropy of the substance increases (Carbonates are an exception! Carbonates interact with water and actually bring MORE order to the system.)
- When a gas molecule escapes from a solvent, the entropy increases
- Entropy generally increases with increasing molecular complexity (crystal structure: KCl vs. $CaCl_2$) since there are more MOVING electrons!
- Reactions increasing the number of moles of particles often increase entropy.

Thermodynamics Topic#5 - Entropy Sample Problems WS#4

1. For each of the following pairs, choose the substance with the higher positional entropy (per mole) at a given temperature.

   a. Solid CO_2 and gaseous CO_2

   b. N_2 gas at 1 atm and N_2 gas at 1.0×10^{-2} atm

2. Predict the sign of the entropy change for each of the following processes. Justify your answer.

   a) sugar is added to water to form a solution. $+ \Delta S$

   b) Iodine vapor condenses on a cold surface to form crystals. $-\Delta S$

Entropy (S)   **Topic#5**

BIG MOMMA (verse 2): $\Delta S^{o}_{rxn} = \sum \Delta S^{o}_{products} - \sum \Delta S^{o}_{reactants}$

Calculating Entropy from Tables of Standard Values

ΔS is (+) when dispersal/disorder increases (favored)

ΔS is (-) when dispersal/disorder decreases

Note: units are usually J/mol$_{rxn}$·K (NOT kJ!)

3. Calculate the entropy change at 25°C, in J/mol$_{rxn}$·K for

$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$ Given the following ΔS data:

3 mol gas → 2 moles gas

$SO_2(g)$	248.1
$O_2(g)$	205.3
$SO_3(g)$	256.6

Ans: -188.3J/mol$_{rxn}$·K

$\Delta S_{rxn} = \sum \Delta S^{\circ}_{prod} - \sum \Delta S^{\circ}_{react}$

$= (2SO_3) - [(2SO_2) + (O_2)]$

$= 2(256.6) - (2(248.1) + 205.3)$

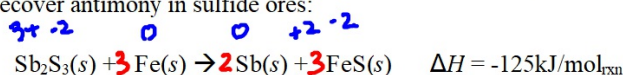$= 513.2 - 701.5 = \boxed{-188.3 \text{ J/mol}_{rxn} \cdot K}$

$\boxed{\Delta S < 0}$

Entropy (S)

$$\Delta S_{surroundings} = \frac{\text{heat transferred}}{\text{temperature at which change occurs}} = \frac{q}{T} = \frac{-\Delta H}{T} \text{ expressed in } \frac{J}{mol_{rxn} \cdot K}$$
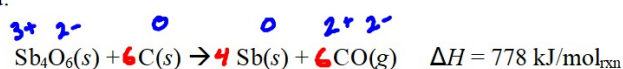
4) In the metallurgy of antimony, the pure metal is recovered via different reactions, depending on the composition of the ore.
   For example, iron is used to recover antimony in sulfide ores:

Sb_2S_3 - oxidizing agent
Fe - reducing agent

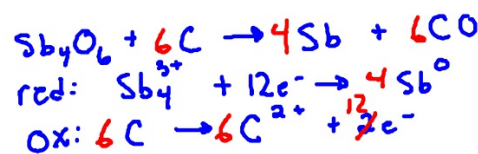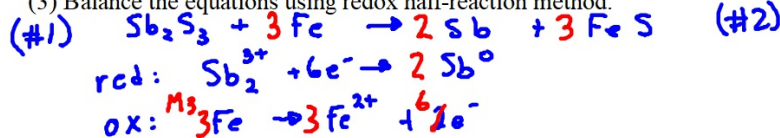$$\overset{3+\ -2}{Sb_2S_3(s)} + \mathbf{3}\overset{0}{Fe(s)} \rightarrow \mathbf{2}\overset{0}{Sb(s)} + \mathbf{3}\overset{+2\ -2}{FeS(s)} \qquad \Delta H = -125 kJ/mol_{rxn}$$

   In oxide ores, carbon is used:

Sb_4O_6 - oxidizing agent
(reduced)

$$\overset{3+\ 2-}{Sb_4O_6(s)} + \mathbf{6}\overset{0}{C(s)} \rightarrow \mathbf{4}\overset{0}{Sb(s)} + \mathbf{6}\overset{2+\ 2-}{CO(g)} \qquad \Delta H = 778\ kJ/mol_{rxn}$$

C - reducing agent

   (1) Identify the reducing and oxidizing agent in each reaction.
   (2) What is the oxidation number for Sb in each of the reactions. 3^+ & 3^+

   (3) Balance the equations using redox half-reaction method.

(#1) $\quad Sb_2S_3 + 3Fe \rightarrow 2Sb + 3FeS$

$\quad$ red: $Sb_2^{3+} + 6e^- \rightarrow 2Sb^0$

$\quad$ ox: $^{M3}3Fe \rightarrow 3Fe^{2+} + {}^6 6e^-$

(#2) $\quad Sb_4O_6 + 6C \rightarrow 4Sb + 6CO$

$\quad$ red: $Sb_4^{3+} + 12e^- \rightarrow 4Sb^0$

$\quad$ ox: $6C \rightarrow 6C^{2+} + {}^{12}\cancel{7}e^-$

   (4) Calculate ΔS_{surr} for each of these reactions at 25°C and 1atm.

(#1) $\quad \dfrac{\Delta S}{(J/mol \cdot K)} = \dfrac{-\Delta H}{T} = \dfrac{-(-125\ kJ/mol)(1000\frac{J}{kJ})}{(273+25)} = \boxed{419\ \dfrac{J}{mol \cdot K}}$

(#2) $\quad \Delta S = \dfrac{-\Delta H}{T} = \dfrac{-(778)(1000)}{298} = \boxed{-2.61 \times 10^3\ \dfrac{J}{mol \cdot K}}$

Ans: 419J/mol$_{rxn}$·K and -2.61x10³J/mol$_{rxn}$·K

Entropy (S)

Entropy Summary

$+\Delta S$ = more dispersal (disorder)

$-\Delta S$ = less dispersal

How does a reaction occur spontaneously?

Since heat will flow between system and surroundings we can use this equation:

$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings}$

$+\Delta S$ then reaction is thermodynamically favorable

$-\Delta S$ then reaction is NOT thermodynamically favorable

Consider the reaction: $2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$ (when ignited reaction is fast and very exothermic!)

ΔS = -88.9 J/mol$_{rxn}$·K and ΔH = -483.6 kJ/mol

1) Why is ΔS negative? *reaction produces 2 moles of gas from 3 moles of reactants. so ΔS < 0*

2) Why is this reaction thermodynamically favorable? *A very large negative enthalpy (exothermic*

1st Law of Thermodynamics - energy is transferred *from* the system *to* the surroundings (and vis-a-versa)

$\Delta S_{surroundings} = \dfrac{\Delta H_{surroundings}}{T} = \dfrac{-\Delta H_{system}}{T}$ $= -\dfrac{(-483.6)(1000)}{298} = \boxed{1623\ J/mol \cdot K}$

Solve for ΔS_{univ}:

$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings}$ $= (-88.9) + (1623) = 1534.1\ \dfrac{J}{mol \cdot K}$

Even though there is a decrease in entropy the reaction is so exothermic it is spontaneous.

Conclusion: very exothermic reactions are spontaneous regardless of a negative entropy change.

Entropy (_S_)

5. At what temperature is the following process spontaneous at 1 atm? $Br_2(l) \rightarrow Br_2(g)$, $\Delta H^o = 31.0kJ/mol$ and

$\Delta S^o = 93.0J/K$-mol. What is the normal boiling point of liquid Br_2? (Ans: 333k)

Gun

$\Delta H^\circ = 31.0\ KJ/mol$

$\Delta S^\circ = 93.0\ J/K\cdot mol$

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

$$\Delta S = \frac{-\Delta H}{T}$$

NTK

$$\Delta S_{r \cdot n} = \frac{\Delta H}{T}$$

UNK

$T = \underline{\qquad}\ K$

Solve:

$$\frac{93.0\ J}{K\cdot mol} = \frac{(31.0\ KJ/mol)(1000\ J/KJ)}{T}$$

$$T = \frac{(31.0 \times 10^3\ J/mol)}{93\ J/K\cdot mol} = \boxed{333\ K}$$

Entropy (S)

6. (OYO) Calculate the thermodynamic boiling point of water given the following information:

$$H_2O(l) \rightarrow H_2O(g)$$
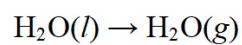
$\Delta H_{vap} = 44\text{kJ/mol}_{rxn}$, and $\Delta S_{vap} = 118.8$ J/mol-K$_{rxn}$. (Ans: 370K)

Entropy (S)

7. Predict the sign of ΔS^o for each of the following reactions: 1 mol   1 mol   1 mol

   a. The thermal decomposition of solid calcium carbonate: $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$ $\Delta S > 0$

   b. The oxidation of SO_2 in air: $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$ $\Delta S^o < 0$
                                              2 mol   1 mol   2 mol

(a) $+ \Delta S$ 1 mol (s) $\rightarrow$ 1 mol (s) + 1 mol (g)

(b) $- \Delta S$ 3 moles (g) $\rightarrow$ 2 moles (g)
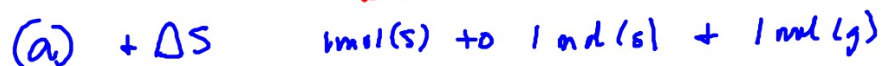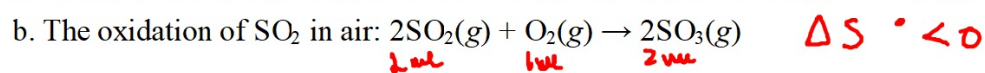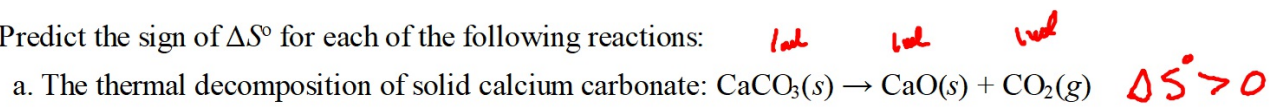
Entropy (_S_)

8. Calculate ΔS° at 25°C for the reaction $2NiS(s) + 3O_2(g) \rightarrow 2SO_2(g) + 2NiO(s)$ given the following standard entropy values: S° (SO_2) = 248J/K-mol, S° (NiO) = 38J/K-mol, S° (O_2) = 205J/K-mol, and S° (NiS) = 53J/K-mol. (Ans: -149J/K)

Gvn
ΔS values

NTK
$\Delta S_{rxn} = \Sigma \Delta S_{prod} - \Sigma \Delta S_{react}$

UNK
$\Delta S_{rxn} = \dfrac{-149}{} \dfrac{J}{mol \cdot K}$

Solve:
$\Delta S_{rxn} = (2SO_2 + 2NiO) - (2NiS + 3O_2)$
$\Delta S_{rxn} = [2(248) + 2(38)] - [2(53) + 3(205)]$
$= 572 - 721 = \boxed{-149 \ J/mol \cdot K}$

Entropy (S)

9. (OYO) Calculate the ΔS^{o} for the reduction of aluminum oxide by hydrogen gas:

$$Al_2O_3(s) + 3H_2(g) \rightarrow 2Al(s) + 3H_2O(g).$$
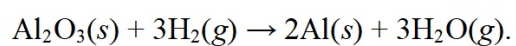
Use the following standard entropy values: S^{o} (Al_2O_3) = 51J/K-mol,

S^{o} (H_2) = 131J/K-mol, S^{o} (Al) = 28J/K-mol, and S^{o} (H_2O) = 189J/K-mol. (Ans: 179J/K)

Free Energy (G)

What is Free Energy (Ans: Sunlight HaHaHaHaHa!)?

- The value of Gibbs Free energy, ΔG, decides whether a reaction is thermodynamically favorable or not.
  - $-\Delta G$ indicates thermodynamically favorable
  - $+\Delta G$ indicates thermodynamically unfavorable

Two methods to solve for ΔG

- "Big Momma" Equation (verse 3), $\Delta G^{o}_{rxn} = \sum G^{o}_{products} - \sum G^{o}_{reactants}$
  - need a table of ΔG^{o} values for the compounds
    - the ΔG^{o} values for elements in their standard state is 0kJ/mol
  - answer is in kJ/mol$_{rxn}$
- "Grand Daddy" equation: $\Delta G^{o}_{rxn} = \Delta H^{o} - T\Delta S^{o}$ $(\Delta S \times 10^{-3})$
  - Remember: ΔH^{o} is in kJ while ΔS^{o} is in J, convert J into kJ by adding (x10^{-3}) to value of ΔS^{o} and changing label to kJ
  - Questions regarding free energy will more than likely require you to calculate ΔH^{o} through Hess's law, calorimetry, or use of a table and Big Momma verse1.
  - At equilibrium ΔG^{o} is equal to 0, so equation becomes $T = \Delta H^{o}/\Delta S^{o}$. This would be the temperature at which a substance changes state under normal conditions (a question on bp can be asked in a thermodynamics question).
- You can use Hess's Law to calculate ΔG^{o}.
- "Rat Link" equation
  - Used to calculate K from ΔG^{o}
  - $\Delta G^{o} = -RT\ln K$ (where $R = 8.31$ J/mol·K and $\Delta G^{o} = 0$ at equilibrium)

Free Energy (*G*)

Relationship Between ΔG°, ΔH°, *T*, and ΔS°

- $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$
- Any exothermic reaction ($-\Delta H^\circ$) that increases in dispersal ($+\Delta S^\circ$) is ALWAYS thermodynamically favorable!
- Any endothermic reaction ($+\Delta H^\circ$) that decreases in dispersal ($-\Delta S^\circ$) is ALWAYS thermodynamically non-favorable!
- An endothermic reaction ($+\Delta H^\circ$) that increases in dispersal ($+\Delta S^\circ$) is thermodynamically favorabale at HIGH termperatures. Non-thermodynamically favoarble at LOW temperatures.
- An exothermic reaction ($-\Delta H^\circ$) that decreases in dispersal ($-\Delta S^\circ$) is thermodynamically favorabale at LOW termperatures. Non-thermodynamically favoarble at HIGH temperatures.

ΔH	ΔS	-TΔS	ΔG	Spontaneity
+	-	+	+	Nonspontaneous
-	+	-	-	Spontaneous
-	-	+	+ or -	Low Temp: Spontaneous High Temp: Nonspontaneous
+	+	-	+ or -	Low Temp: Nonspontaneous High Temp: Spontaneous

Free Energy (G)

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

1. $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$
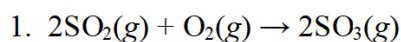
The above reaction was carried out at 25°C and 1atm. Calculate ΔH°, ΔS°, and ΔG° using the following data: (Ans: -198 kJ/mol$_{rxn}$, -187 J/K-mol, and -142kJ/mol$_{rxn}$)

Gvn

ΔH Data
ΔS Data
$T = 273 + 25 = 298 K$

NTK

$\Delta G = \Delta H - T\Delta S$
$\Delta H = \Sigma H_{prod} - \Sigma H_{react}$
$\Delta S = \Sigma S_{prod} - \Sigma S_{react}$

UNK

$\Delta G = \underline{\qquad} KJ/mol$

Solve: $\Delta H = 2SO_3 - (2SO_2 + O_2) = (2(-396)) - (2(-297) + 0)$

$\Delta H = \boxed{-198 \ KJ/mol}$

$\Delta S = 2SO_3 - (2SO_2 + O_2) = (2(257)) - (2(248) + 205)$

$\Delta S < 0, \quad \Delta S = \boxed{-187 \ J/K \cdot mol}$

$\Delta G = (-198) - (298)(-187 \times 10^{-3}) = \boxed{-142 \ KJ/mol}$

Free Energy (_G_)
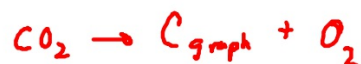
2. Using the following data (at 25°C): $C_{diamond}(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta G° = $ -397kJ and $C_{graphite}(s) + O_2(g) \rightarrow$ CO_2(g)$ $\Delta G° = $ -394kJ. Calculate ΔG for the reaction: $C_{diamond}(s) \rightarrow C_{graphite}(s)$ (Ans: -3kJ)

-reversed

Hess's Law

Solve:

$C_{dia} + O_2 \rightarrow CO_2$ $\Delta G = -397$

$CO_2 \rightarrow C_{graph} + O_2$ $\Delta G = -(-394)$

_____

$C_{dia} \rightarrow C_{graphite}$

$\Delta G_{rxn} = \Delta G_{dia} + (-\Delta G_{grap})$

$= -397 + (-(-394)) = \boxed{-3 \, kJ}$

Free Energy (G)

3. Calculate the free energy of reaction for the oxidation of water to produce hydrogen peroxide given the following information: $2H_2O(l) + O_2(g) \rightarrow 2H_2O_2(l)$
ΔG_f values: $H_2O(l)$ = -56.7 kcal/mol$_{rxn}$, $O_2(g)$ = 0 kcal/mol$_{rxn}$, and $H_2O_2(l)$ = -27.2 kcal/mol$_{rxn}$
(Ans: 59kcal/mol$_{rxn}$)

Big Momma
Eg. verse 3

$\Delta G^{\circ}_{rxn} = \Sigma \Delta G^{\circ}_{f\ prod} - \Sigma \Delta G^{\circ}_{f\ react}$

$= [2\ H_2O_2(l)] - [2H_2O(l) + O_2(g)]$

$= 2(-27.2) - (2(-54.7) \pm 0)$

$= -54.4 + 113.4 = 59\ Kcal/mol\ rxn$

4. (OYO) Methanol is a high-octane fuel used in high-performance racing engines. Calculate ΔG° for the reaction $2CH_3OH(g) + 3O_2(g) \rightarrow 2CO_2(g) + 4H_2O(g)$ given the following free energies of formation: ΔG°_f ($CH_3OH(g)$) = -163kJ/mol, ΔG°_f (O_2) = 0kJ/mol, ΔG°_f (CO_2) = -394kJ/mol, and ΔG°_f (H_2O) = -229kJ/mol.   (Ans: -1378kJ)

Free Energy (G)

5. (OYO) A chemical engineer wants to determine the feasibility of making ethanol (C_2H_5OH) by reacting water with ethylene (C_2H_4) according to the equation $C_2H_4(g) + H_2O(l) \rightarrow C_2H_5OH(l)$. Is this reaction spontaneous under standard conditions? Given data: ΔG°_f (C_2H_5OH) = -175kJ/mol, ΔG°_f (H_2O) = -237kJ/mol, and ΔG°_f (C_2H_4) = 68kJ/mol. (Ans: -6kJ, yes)

Free Energy (*G*) (Non-Standard Conditions)   Topic#5

ΔG° - standard conditions

ΔG - nonstandard conditions

Free Energy (*G*) at Non-Standard Conditions

- The change in Free Energy at non-standard condictions is represented by ΔG
- The equation to use is $\Delta G = \Delta G^{\circ} + RT\ln Q$ where R is 8.31×10^{-3} kJ (it is really 8.31 but we are using ΔG and ΔG is in kJ/mol.

6. One method of synthesizing methanol (CH_3OH) involves reacting carbon monoxide with hydrogen gas:

$CO(g) + 2H_2(g) \rightarrow CH_3OH(l)$. Calculate ΔG at 25°C for this reaction where carbon monoxide gas at 5.0atm and hydrogen gas at 3.0atm are converted to liquid methanol. Given data: ΔG°_f of ($CH_3OH(l)$) = -166 kJ/mol, ΔG°_f of (H_2) = 0 kJ/mol, and ΔG°_f of (CO) = -137 kJ/mol. (Ans: ΔG° = -29kJ/mol, ΔG = -38kJ/mol)

Gun

$P_{CO} = 5.0\, atm$

$P_{H_2} = 3.0\, atm$

ΔG°_f data

Solve:

$Q = \dfrac{1}{(P_{CO})(P_{H_2})^2}$

✱ no (l) or (s) in reaction quotient

NTK

$\Delta G^{\circ}_{rxn} = \Sigma G^{\circ}_{f\,(prod)} - \Sigma G^{\circ}_{f\,(react)}$

$\Delta G = \Delta G^{\circ} + RT\ln Q$ ($R = 8.31 \times 10^{-3}$ kJ)

$\Delta G = (CH_3OH) - (CO + 2H_2)$

$= (-166) - (-137) = \boxed{-29\ kJ/mol}$

$\Delta G = -29 + (8.31\times10^{-3})(298)\left(\ln \dfrac{1}{(5.0)(3.0)^2}\right)$

$= -29 + (-9.43)$

$= -38.43 = \boxed{-38\ kJ/mol}$

Free Energy (*G*) and *K*

use $\Delta G = -RT \ln K$

7. Given $K = 2.81 \times 10^{-16}$ for a following reaction: $Cu^{2+}(aq) + Ag(s) \rightleftharpoons Cu(s) + 2Ag^{+}(aq)$

Find ΔG^o.   (Ans: 88.7kJ)

GIVN

NTK
$\Delta G = \Delta G^{\circ} + RT \ln K$
$\Delta G = 0$
$\Delta G^{\circ} = -RT \ln K$

UNK
$\Delta G = \underline{\hspace{2cm}} kJ$

Solve: $\Delta G^{\circ} = -(8.31)(298) \ln(2.81 \times 10^{-16})$
$= -(8.31)(298)(-35.808177)$
$= +88,675 \, J = 8.87 \times 10^{4} \, J$
$= \boxed{88.7 \, kJ}$

Free Energy (G) and K

$\Delta G = \Delta G^\circ + RT\ln Q$

8. Consider the ammonia synthesis reaction $N_2(g) + 3H_2(g) \leftrightarrow 2NH_3(g)$ where $\Delta G^\circ = $ -33.3kJ/mol of N_2

consumed at 25°C. For each of the following mixtures of reactants and products at 25°C, predict the

direction in which the system will shift to reach equilibrium.

    a. $P_{NH3} = $ 1.00atm, $P_{N2} = $ 1.47atm, $P_{H2} = $ 1.00x10^{-2}atm (Ans: no shift)

    b. $P_{NH3} = $ 1.00atm, $P_{N2} = $ 1.00atm, $P_{H2} = $ 1.00atm (Ans: shift to the right, more products need to be

    formed)

<u>Gun</u>

$P_{NH_3} = 1.00\,atm$

$P_{N_2} = 1.47\,atm$

$P_{H_2} = 1.00 \times 10^2\,atm$

$\Delta G^\circ = -33.3\,^{kJ}/_{mol}$

$Q = \dfrac{(P_{NH_3})^2}{(P_{N_2})(P_{H_2})^3}$

<u>NTK</u>

$\Delta G = \Delta G^\circ + RT\ln Q$

$\Delta G > 0$ shift left

$\Delta G < 0$ Shift right

$\Delta G = 0$ no shift

<u>Solve:</u>

$\Delta G = (-33.3) + (8.31 \times 10^{-3})(298)\left(\ln \dfrac{(1.0)^2}{(1.47)(0.01)^3}\right)$

$\Delta G = (-33.3) + (8.31 \times 10^{-3})(298)(13.4)$

$= (-33.3) + (33.2) = 0$

$\Delta G = 0$ (no shift)

<u>UnK</u>

$\Delta G = 0$

shift : <u>none</u>

If $\Delta G < 0$, then reaction shifts right .

If $\Delta G > 0$, then reaction shifts left.

If $\Delta G = 0$, then reaction is at equilibrium, so no shift.

Free Energy (G) and K

$$\Delta G = \Delta G^\circ + RT\ln Q$$

8. Consider the ammonia synthesis reaction $N_2(g) + 3H_2(g) \leftrightarrow 2NH_3(g)$ where $\Delta G^\circ = -33.3kJ/mol$ of N_2 consumed at 25°C. For each of the following mixtures of reactants and products at 25°C, predict the direction in which the system will shift to reach equilibrium.

    a. $P_{NH3} = 1.00$atm, $P_{N2} = 1.47$atm, $P_{H2} = 1.00\times10^{-2}$atm (Ans: no shift)

    b. $P_{NH3} = 1.00$atm, $P_{N2} = 1.00$atm, $P_{H2} = 1.00$atm (Ans: shift to the right, more products need to be formed)

(b)

Gun

$P_{NH_3} = 1.00$ atm

$P_{N_2} = 1.00$ atm

$P_{H_2} = 1.00$ atm

$\Delta G^\circ = -33.3$ kJ/mol

$Q = \dfrac{(P_{NH_3})^2}{(P_{N_2})(P_{H_2})^3}$

NTK

$\Delta G = \Delta G^\circ + RT\ln Q$

$\Delta G > 0$ shift left

$\Delta G < 0$ shift right

$\Delta G = 0$ no shift

UnK

$\Delta G < 0$

shift: **right**

Solve:

$\Delta G = (-33.3) + (8.31\times10^{-3})(298)\left(\ln \dfrac{(1)^2}{(1)(1)^3}\right)$

$\Delta G = (-33.3) + (8.31\times10^{-3})(298)(0)$

$= (-33.3) + (0) = -33.3$

$\Delta G < 0$ (shifts right; rxn makes more products)

If $\Delta G < 0$, then reaction shifts right.
If $\Delta G > 0$, then reaction shifts left.
If $\Delta G = 0$, then reaction is at equilibrium, so no shift.

Free Energy (*G*) and *K*

If $\Delta G < 0$, then reaction shifts right .
If $\Delta G > 0$, then reaction shifts left.
If $\Delta G = 0$, then reaction is at equilibrium, so no shift.

Free Energy (G)

9. The overall reaction for corrosion (rusting) of iron by oxygen is: $4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$. Using the following data, calculate the equilibrium constant for this reaction at 25°C. (Ans: e^{601} or 10^{261})

Gvn

$T = 25°C = 298 K$

NTK

$\Delta H°_{rxn} =$

$\Delta S°_{rxn} =$

$\Delta G°_{rxn} =$

$K = e^{-\Delta G/2.48}$

Substance	$\Delta H_f°$ (kJ/mol)	S° (J/K · mol)
$Fe_2O_3(s)$	−826	90
$Fe(s)$	0	27
$O_2(g)$	0	205

UNK

$K = \dfrac{e^{601}}{}$

Solve:

$\Delta H° = (2(Fe_2O_3)) - (4Fe + 3O_2^°)$

$\Delta H° = 2(-826) = \boxed{-1652 \text{ kJ}}$

$\Delta S° = [2(Fe_2O_3)] - [4Fe + 3O_2]$

$\Delta S° = [2(90)] - [4(27) + 3(205)]$

$= (180 - 108 - 615) = \boxed{-543 \text{ J}}$

$\Delta G = \Delta H - T\Delta S = (-1652) - (298)(-543 \times 10^{-3})$

$= \boxed{-1490.2 \text{ kJ}} \quad (KJ)$

$K = e^{-\Delta G/2.48} = e^{-(-1490)/2.48}$

$= e^{601}$

$\boxed{K = e^{601}}$

(KJ)

Free Energy (_G_) and _E°_cell

Solving for Δ_G_ using the "minus numfe" equation

- electrochemistry ($E°_{cell}$); $E°_{cell} = E_{red} + E_{ox}$
- $\Delta G = -nFE°$
  - where n is the number of electrons transferred
  - where F is Faraday's constant: 1 mole $e^- = 96,485$ Coloumbs
  - where $E°$ is the standard cell potential
    Note: 1 volt = 1J/C

10. Using these coupled reactions:

    $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ $E_{red} = -0.763V$, $E_{ox} = -(-0.763) = 0.763$
    $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$ $E_{red} = 0.340V$
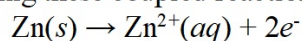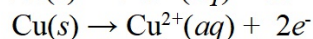
    a. Identify the anode and cathode.
    b. Find the $E°_{cell}$.   (Ans: 1.103V)
    c. Calculate $\Delta G°$.
    d. Calculate K.

    Gun
    Redox equations

    Anode: Zn
    (Anox)

    Cathode: Cu
    (redox)

    <u>Solve:</u>   <u>UNK</u>

    (B) $E°_{cell} = E_{red} + E_{ox} = 0.34 + 0.763$
                       $= 1.103V$

    (C) $\Delta G = -nFE° = -(2)(96,480)(1.103) = -212834 J$
                          $-(-213/2.48)$ ($\sim 213 KJ$)

    (D) $K = e^{-\Delta G/2.48} = e^{-(-213/2.48)}$
                       $= e^{+85.89} = \boxed{2.0 \times 10^{37}}$