AP* Chemistry
Spontaneity: Entropy and Free Energy

WHAT DRIVES A REACTION TO BE SPONTANEOUS?

(1) **ENTHALPY (ΔH)** – heat content (exothermic reactions are generally favored)
(2) **ENTROPY (ΔS)** – disorder of a system (more disorder is favored) Nature tends toward chaos! Think about your room at the end of the week! Your mom will love this law.


A disordered pile of playing cards.

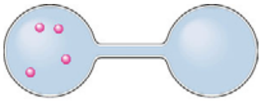
Spontaneous reactions are those that occur without outside intervention. They may occur fast OR slow (that is kinetics). Some reactions are very fast (like combustion of hydrogen) other reactions are very slow (like graphite turning to diamond)

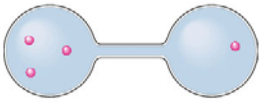
ENTROPY:

<u>**The second law of thermodynamics:**</u> the universe is constantly increasing disorder. Rudolph Clausius (you'll hear lots about him later when we study vapor pressures) "discovered" it and gave it its symbol.)

<u>**The third law of thermodynamics:**</u> the entropy of a perfect crystal at 0K is zero.
[not a lot of perfect crystals out there so, entropy values are RARELY ever zero—even elements]
So what? This means the absolute entropy of a substance can then be determined at any temp. higher than 0 K. (Handy to know if you ever need to defend *why* G & H for elements = 0. . . . BUT S does not!)

Predicting the entropy of a system based on physical evidence:


Arrangement I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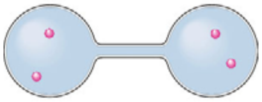

Arrangement III

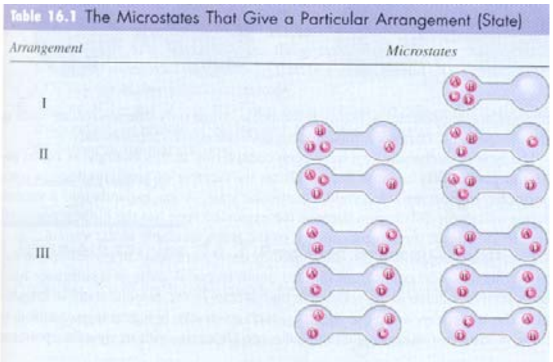


Table 16.1 The Microstates That Give a Particular Arrangement (State)

1) The greater the disorder or randomness in a system, the larger the entropy.
2) The entropy of a substance always increases as it changes from solid to liquid to gas.
3) When a pure solid or liquid dissolves in a solvent, the entropy of the substance increases (carbonates are an exception!--they interact with water and actually bring MORE order to the system)
4) When a gas molecule escapes from a solvent, the entropy increases
5) Entropy generally increases with increasing molecular complexity (crystal structure: KCl vs $CaCl_2$) since there are more MOVING electrons!

6) Reactions increasing the number of moles of particles often increase entropy**.**

☛ In general, the greater the number of arrangements, the higher the entropy of the system!

Exercise 2 **Predicting Entropy Changes**

Predict the sign of the entropy change for each of the following processes.

A: Solid sugar is added to water to form a solution.
B: Iodine vapor condenses on a cold surface to form crystals.

Calculating Entropy from tables of standard values: (Just the same as calculating the enthalpy earlier)

Sample Problem A:

Which of the following has the **largest** increase in entropy?

a) $CO_{2(s)} \rightarrow CO_{2(g)}$
b) $H_{2(g)} + Cl_{2(g)} \rightarrow 2\ HCl_{(g)}$
c) $KNO_{3(s)} \rightarrow KNO_{3(l)}$
d) $C_{(diamond)} \rightarrow C_{(graphite)}$

BIG MAMMA, verse 2: $\Delta S°_{rxn} = \Sigma\ \Delta S°_{(products)} - \Sigma\ \Delta S°_{(reactants)}$

S is + when disorder increases (favored)
S is – when disorder decreases
Units are usually J/K• mol (**not** kJ ---tricky!)

Sample Problem B:

Calculate the entropy change at 25°C, in J/K for:

$$2\ SO_{2(g)} + O_{2(g)} \rightarrow 2\ SO_{3(g)}$$

Given the following data:

$SO_{2(g)}$	248.1 J/K• mol
$O_{2(g)}$	205.3 J/K•mol
$SO_{3(g)}$	256.6 J/K• mol

Answer: -188.3 J/K

ENTROPY CHANGES FOR REVERSIBLE PHASE CHANGES ☞ that's a phase change at constant temperature

- $$\Delta S = \frac{\text{heat transferred}}{\text{temperature at which change occurs}} = \frac{q}{T}$$

  **where the heat supplied (endothermic) ($q > 0$) or evolved (exothermic) ($q < 0$) is divided by the temperature in Kelvins
  ** It is important here to note if the reaction is endothermic or exothermic. The actual significance of this is really dependent on the temperature at which the process occurs.
  (i.e., If you gave a millionaire $100 it would not make much difference in his happiness; if you gave a poor college student $100 it would create a totally different expression of happiness!)

  EX: water (l @ 100) → water (g @ 100)
  the entropy will increase

- Taking favored conditions into consideration, the equation above rearranges into:

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

- Give signs to ΔH following exo/endo guidelines! (If reaction is exo.; entropy of system increases—makes sense!)

Exercise 4 **Determining ΔS_{surr}**

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 reduce antimony in sulfide ores:

$$Sb_2S_3(s)+3Fe(s)\rightarrow 2Sb(s)+3FeS(s) \qquad \Delta H = -125\text{kJ}$$

Carbon is used as the reducing agent for oxide ores:

$$Sb_4O_6(s)+6C(s)\rightarrow 4Sb(s)+6CO(g) \qquad \Delta H = 778\text{kJ}$$

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

$= -2.61 \times 10^3$ J/K

SUMMARY ENTROPY:
$\Delta S = +$ MORE DISORDER (FAVORED CONDITION)
$\Delta S = -$ MORE ORDER

- Whether a reaction will occur spontaneously *may be* determined by looking at the ΔS of the universe.

  $\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = \Delta S_{\text{universe}}$
  IF $\Delta S_{\text{universe}}$ is +, then reaction is spontaneous
  IF $\Delta S_{\text{universe}}$ is -, then reaction is NONspontaneous

Consider

$2\,H_2\,(g) + O_2\,(g) \rightarrow H_2O\,(g)$ ignite & rxn is fast!

$\Delta S_{\text{system}} = -88.9\text{J/K}$
entropy declines (due mainly to 3→2 moles of gas!)
. . . to confirm we need to know entropy of surroundings

$\Delta S_{\text{surroundings}} = \dfrac{q_{\text{surroundings}}}{T}$ this comes from ΔH calc.

$H_{\text{system}} = -\,483.6\text{ kJ}$

First law of thermodynamics demands that this energy is transferred ***from*** the system ***to*** the surroundings so...

$-\Delta H_{\text{system}} = \Delta H_{\text{surroundings}}$ OR
$-\,(-483.6\text{ kJ}) = +483.6\text{ kJ}$

$$\Delta S^\circ_{\text{surroundings}} = \frac{\Delta H^\circ_{\text{surroundings}}}{T} = \frac{+\,483.6\text{ kJ}}{298\text{ K}} = 1620\text{ J/K}$$

Now we can find $\Delta S^\circ_{\text{universe}}$

$\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = \Delta S_{\text{universe}}$
$(-88.9\text{ J/K}) + (1620\text{ J/K}) = 1530\text{ J/K}$

Even though the entropy of the system declines, the entropy change for the surroundings is SOOO large that the overall change for the universe is positive.

Bottom line: A process is spontaneous in spite of a negative entropy change as long as it is extremely exothermic. ***Sufficient exothermicity offsets system ordering.***

FREE ENERGY

Calculation of Gibb's free energy is what **ultimately** decides whether a reaction is spontaneous or not. ***NEGATIVE ΔG's are spontaneous***. ΔG can be calculated one of several ways:

(a) Big Mamma,verse 3: $\Delta G^\circ_{\text{rxn}} = \Sigma\, \Delta G^\circ_{\text{(products)}} - \Sigma\, \Delta G^\circ_{\text{(reactants)}}$

This works the same way as enthalpy and entropy from tables of standard values! Standard molar free energy of formation--same song, 3rd verse. $\Delta G^\circ_f = 0$ for elements in standard state

(b) $\boxed{\text{GRAND Daddy: } \Delta G = \Delta H - T\Delta S}$

This puts together all information thus far! By far, one of the most beneficial equations to learn for AP exam!

(c) Hess's law summation

Works same as Hess's in the enthalpy section—sum up equations using the guidelines as before.

(d) $\Delta G = \Delta G^\circ + RT\ln(Q)$

Define terms: ΔG = free energy not at standard conditions
ΔG° = free energy at standard conditions
R = universal gas constant 8.3145 J/mol•K
T = temp. in Kelvin
ln = natural log
Q = reaction quotient: (for gases this is the partial pressures of the products divided by the partial pressures of the reactants—all raised to the power of their coefficients) $Q = \frac{[\text{products}]}{[\text{reactants}]}$

(e) $\boxed{\text{“RatLink”: } \Delta G^\circ = -RT\ln K}$

Terms: basically the same as above --- however, here the system is at equilibrium, so $\Delta G = 0$ and K represents the equilibrium constant under standard conditions.
$K = \frac{[\text{products}]}{[\text{reactants}]}$ still raised to power of coefficients

(f) $\boxed{\text{“nFe”: } \Delta G^\circ = -nFE^\circ \quad \textbf{remember this!!}}$

Terms: ΔG° = just like above—standard free energy
n = number of moles of electrons transferred (look at ½ reactions)
F = Faraday's constant 96,485 Coulombs/mole electrons
E° = standard voltage ** one volt = joule/coulomb**

BIG MAMMA, verse 3: $\Delta G^\circ_{rxn} = \Sigma\, \Delta G^\circ_{(products)} - \Sigma\, \Delta G^\circ_{(reactants)}$

Sample Problem C:
Find the free energy of formation for the oxidation of water to produce hydrogen peroxide.

$$2\ H_2O_{(l)} + O_{2(g)} \rightarrow 2\ H_2O_{2(l)}$$

Given the following information:

	ΔG°_f
$H_2O_{(l)}$	-56.7 kcal/mol
$O_{2(g)}$	0 kcal/mol
$H_2O_{2(l)}$	-27.2 kcal/mol

Answer: 59.0 kcal/mol

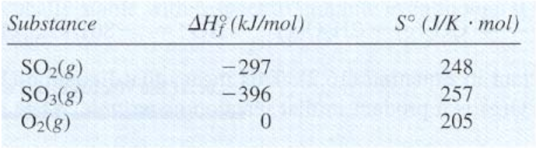
GRAND Daddy: ΔG = ΔH - TΔS

Exercise 9 **Calculating ΔH°, ΔS°, and ΔG°**

Consider the reaction

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

carried out at 25°C and 1 atm. Calculate ΔH°, ΔS°, and ΔG° using the following data:



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

ΔH° = -198 kJ
ΔS° = -187 J/K
ΔG° = -142 kJ

Hess's law of summation

Exercise 10 **Calculating ΔG°**

Using the following data (at 25°C)

$$C_{diamond}(s)+O_2(g)\rightarrow CO_2(g) \quad \Delta G^\circ = -397\text{ kJ} \quad (16.5)$$
$$C_{graphite}(s)+O_2(g)\rightarrow CO_2(g) \quad \Delta G^\circ = -394\text{ kJ} \quad (16.6)$$

Calculate ΔG° for the reaction

$$C_{diamond}(s)\rightarrow C_{graphite}(s)$$

= -3 kJ

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

Exercise 13 **Calculating ΔG°**

One method for synthesizing methanol (CH_3OH) involves reacting carbon monoxide and hydrogen gases:

$$CO(g) + 2H_2(g) \rightarrow CH_3OH(l)$$

Calculate ΔG at 25°C for this reaction where carbon monoxide gas at 5.0 atm and hydrogen gas at 3.0 atm are converted to liquid methanol.

= -38 kJ/mol rxn

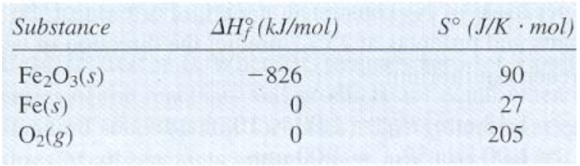
"RatLink": $\Delta G^\circ = -RT\ln K$

Exercise 15 **Free Energy and Equilibrium II**

The overall reaction for the corrosion (rusting) of iron by oxygen is

$$4\,Fe_{(s)} + 3\,O_{2\,(g)} \rightleftarrows 2\,Fe_2O_{3\,(s)}$$

Using the following data, calculate the equilibrium constant for this reaction at 25°C.



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

$K = 10^{261}$

Gibb's equation can also be used to calculate the phase change temperature of a substance. During the phase change, there is an equilibrium between phases so the value of $\Delta G°$ is zero. Really just like what we did earlier in this unit with enthalpy and entropy!

Sample Problem:

Find the thermodynamic boiling point of $H_2O_{(l)} \rightarrow H_2O_{(g)}$

Given the following information:

$H_{vap} = +44$ kJ $S_{vap} = 118.8$ J/K

Answer: 370K

SUMMARY OF FREE ENERGY:

ΔG = + NOT SPONTANEOUS

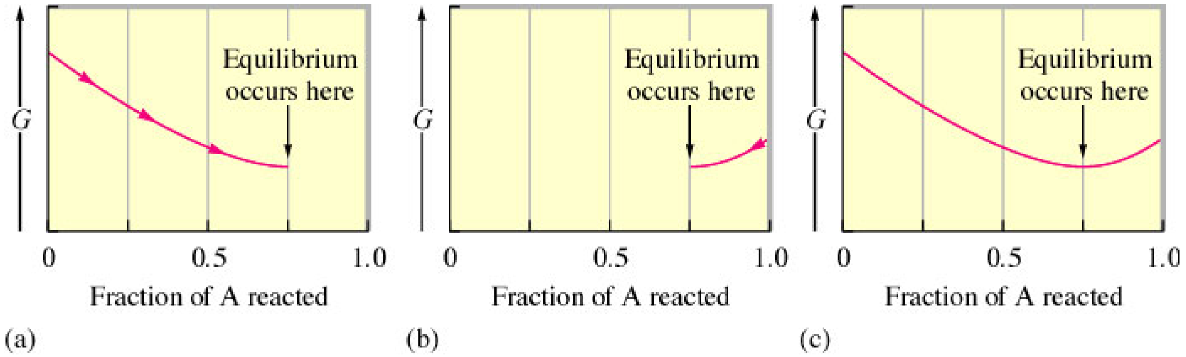
ΔG = - SPONTANEOUS

Conditions of ΔG:

ΔH	ΔS	Result
negative	positive	spontaneous at all temperatures
positive	positive	spontaneous at high temperatures
negative	negative	spontaneous at low temperatures
positive	negative	not spontaneous, ever

Relationship to K and E :

ΔG	K	E
0	at equilibrium; K = 1	0
negative	>1, products favored	positive
positive	<1, reactants favored	negative



Consider the reaction: A (g) ⇄ B (g)

a) The change in free energy to reach equilibrium, beginning with 1.0 mol of A(g) at $P_A = 2.0$ atm
b) The change in free energy to reach equilibrium, beginning with 1.0 mol of B (g) at $P_B = 2.0$ atm.
c) The free energy profile for A (g) ⇄ B (g) in a system containing 1.0 mol (A plus B) at $P_{TOTAL} = 2.0$ atm.

Each point on the curve corresponds to the total free energy of the system for a given combination of A and B.

The value of free energy is not only useful for defining spontaneity. It is also very useful in understanding the maximum amount of work produced or required by a system at constant temperature and pressure:

$$\Delta G = w_{max}$$

When the reaction is spontaneous, **ΔG is the energy available to do work** such as moving a piston or flowing of electrons. When ΔG is positive, and thus non-spontaneous, it represents the amount of work needed to make the process occur.

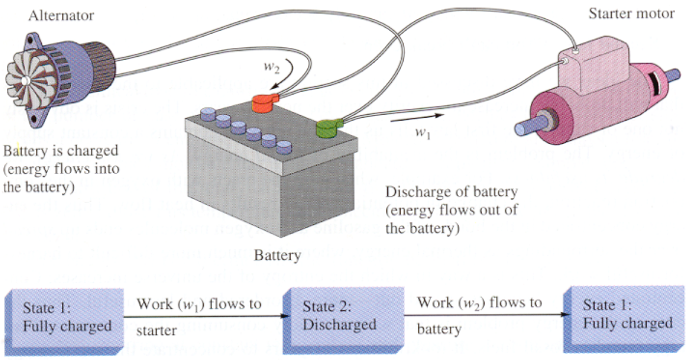


Figure 16.10

A battery can do work by sending current to a starter motor. The battery can then be recharged by forcing current through it in the opposite direction. If the current flow in both processes is infinitesimally small, $w_1 = w_2$. This is a *reversible process.* But if the current flow is finite, as it would be in any real case, $w_2 > w_1$. This is an *irreversible process* (the *universe is different* after the cyclic process occurs). All real processes are irreversible.