Thermodynamic Favorability Entropy and Free Energy

WHAT DRIVES A REACTION TO BE THERMODYNAMICALLY FAVORABLE?

Thermodynamically favored 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 diamond turning to graphite)

What is thermodynamically favored mean/measured?

How do we look at reactions to determine if they are thermodynamically favored or not?

Physical and Chemical Change

Physical and Chemical Change occur in one direction

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

$$\Delta H^\circ = -889 \text{ kJ mol}^{-1}$$

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The reverse reaction does not happen.

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Physical and Chemical Change

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

Is thermodynamically favored

The reverse reaction

$CO_2(g) + 2H_2O(l) \rightarrow CH_4(g) + 2O_2(g)$

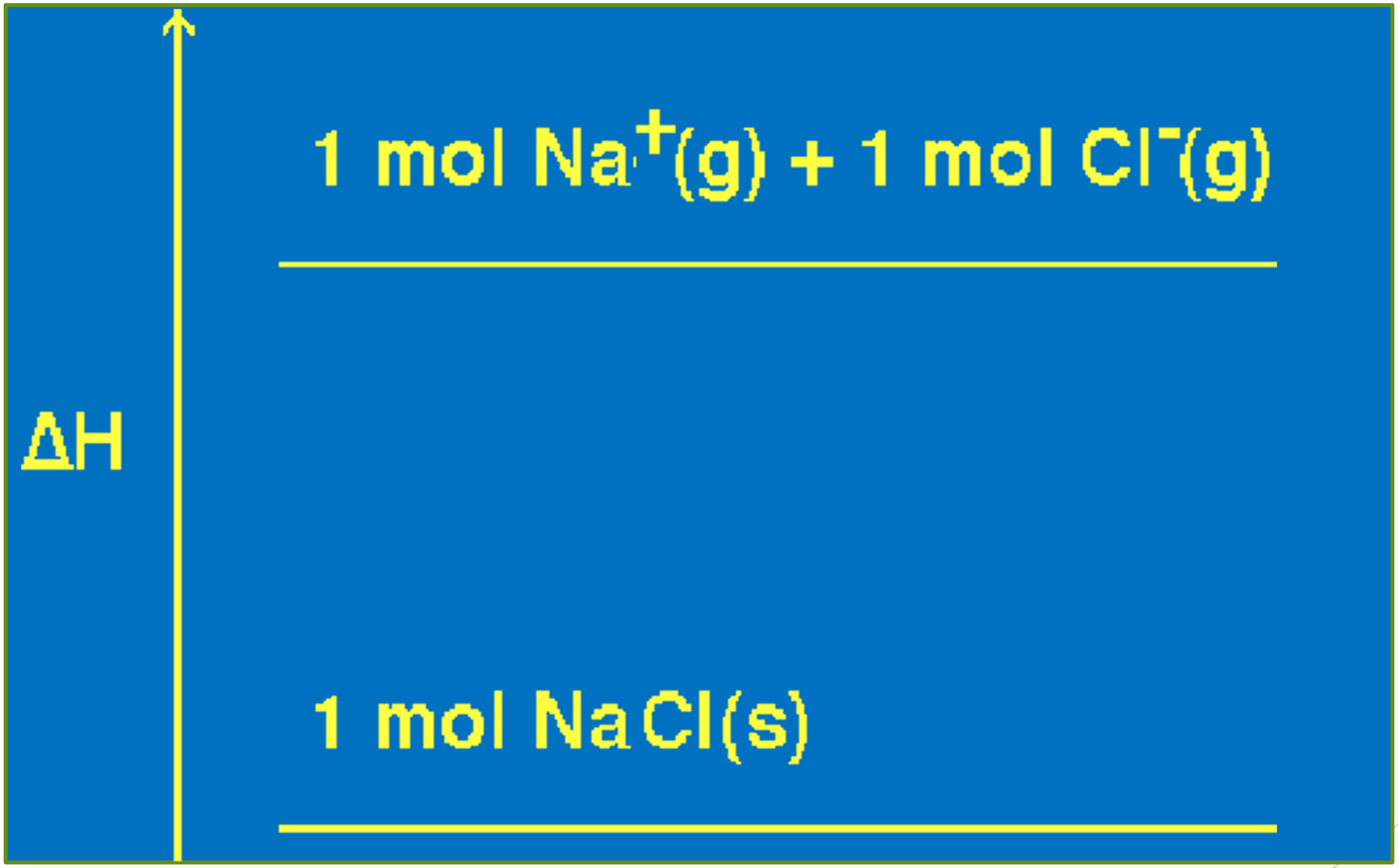
Is not thermodynamically favored

ENTHALPY (ΔH)

heat content

(exothermic reactions are generally favored)

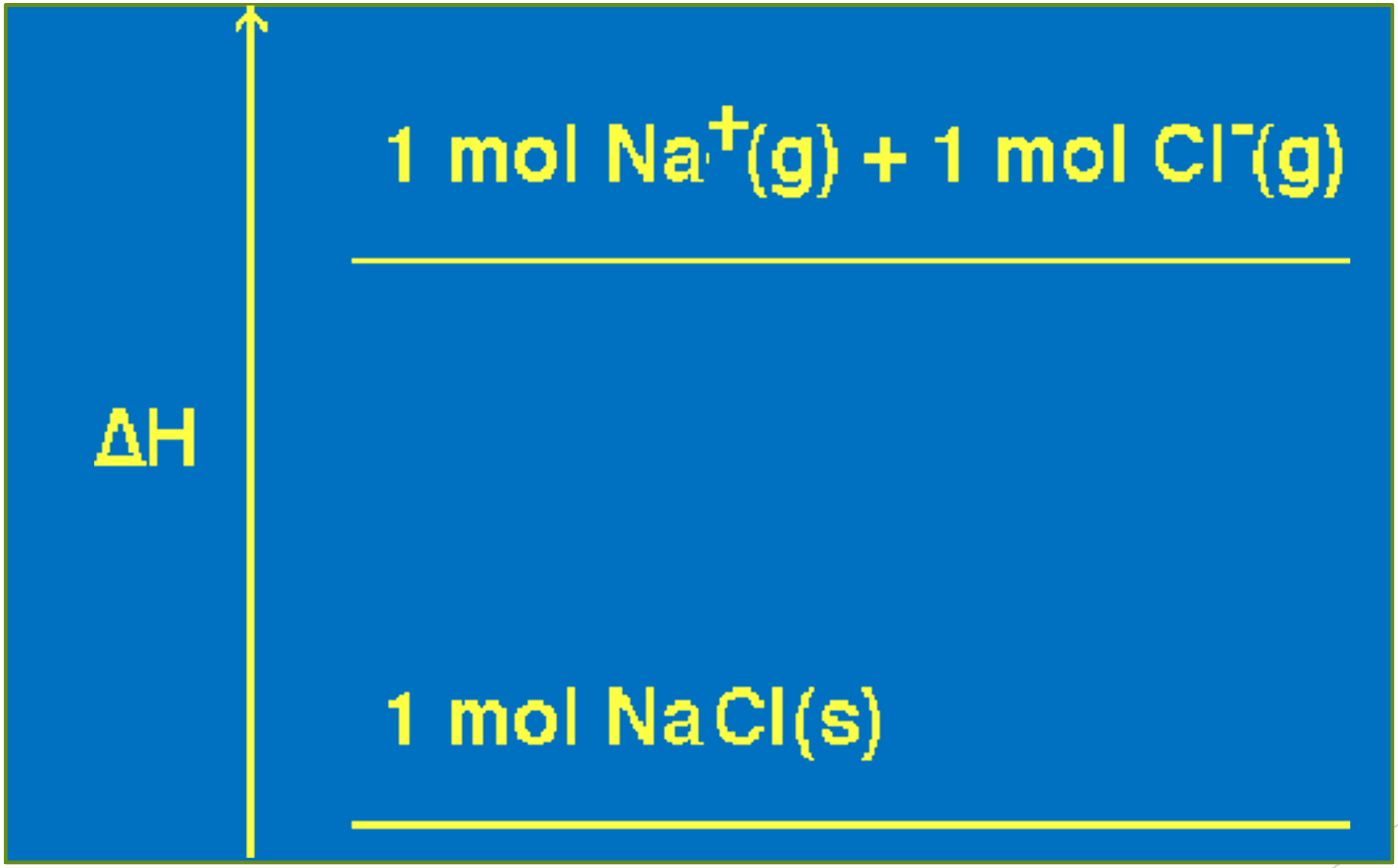
ENTHALPY (ΔH)



How would you write a reaction?

Is the reaction exothermic or endothermic?

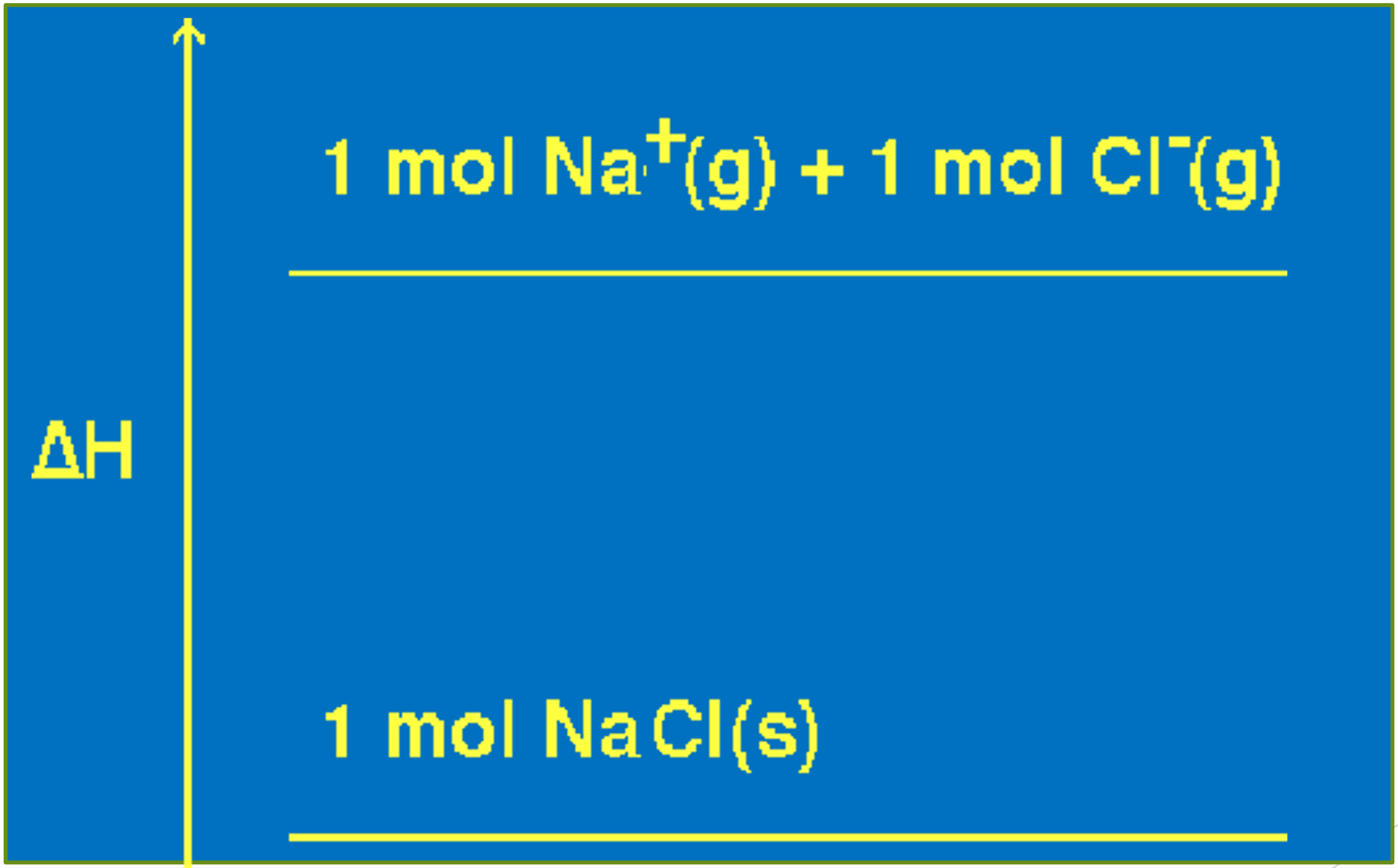
ENTHALPY (ΔH)



$NaCl(s)$ ----> $Na^{+}(g) + Cl^{-}(g)$

$\Delta H = +782\ kJ\ mol^{-1}$

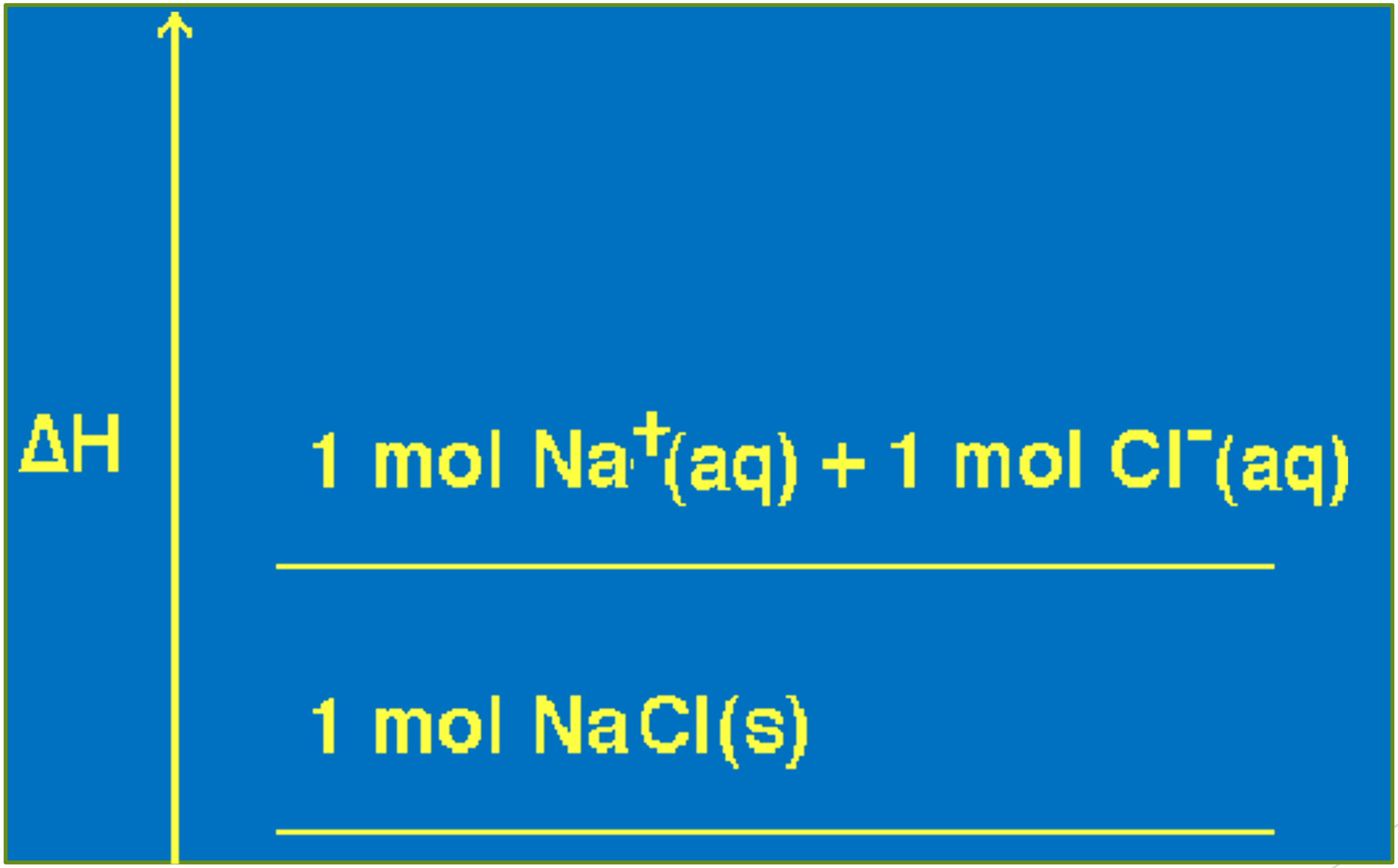
ENTHALPY (ΔH)



$NaCl(s)$ ----> $Na^+(g) + Cl^-(g)$

Why doesn't a crystal of NaCl become $Na^+(g) + Cl^-(g)$?

ENTHALPY (ΔH)



$NaCl(s) \text{ ----> } Na^+(aq) + Cl^-(aq)$

$\Delta H = +3.90 \text{ kJ mol}^{-1}$

ENTHALPY (ΔH)

Predicting ΔH for a reaction:

Phase changes:

Intuition:

ENTHALPY (ΔH)

Predicting ΔH for a reaction:

Phase changes: $H_2O(l) \text{ ---> } H_2O(g)$

Intuition:

$Na(s) + H_2O(l) \text{ ---> } H_2(g) + NaOH(aq)$

$H_2(g) + 1/2O_2(g) \text{ ---> } H_2O(l)$

ENTHALPY (ΔH)

Predicting ΔH for a reaction:

Phase changes: $H_2O(l) \text{ ---> } H_2O(g)$ ΔH = +

Intuition:

$Na(s) + H_2O(l) \text{ ---> } H_2(g) + NaOH(aq)$ ΔH = –

$H_2(g) + 1/2O_2(g) \text{ ---> } H_2O(l)$ ΔH = –

ENTHALPY (ΔH)

Using the following standard enthalpy of reaction data,

$2C(s) + 3H_2(g) \rightarrow C_2H_6(g)$ $\Delta H_f^\circ = -84.68 \text{ kJ mol}^{-1}$

$C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta H_f^\circ = -394 \text{ kJ mol}^{-1}$

$H_2(g) + 1/2O_2(g) \rightarrow H_2O(l)$ $\Delta H_f^\circ = -286 \text{ kJ mol}^{-1}$

Calculate the heat of reaction for the combustion of 1 mol of ethane (C_2H_6).

$C_2H_6(g) + 7/2O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$

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$\Delta H^\circ_{rxn} = \Sigma(m\Delta H_f^\circ(\text{products})) - \Sigma(n\Delta H_f^\circ(\text{reactants}))$

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$\Delta H^\circ_{rxn} = \Sigma(m\Delta H_f^\circ(\text{products})) - \Sigma(n\Delta H_f^\circ(\text{reactants}))$

$\Delta H^\circ_{rxn} = \Sigma(2\cdot\Delta H_f^\circ(CO_2(g)) + 3\cdot\Delta H_f^\circ(H_2O(l)))$

$- (1\cdot \Delta H_f^\circ(C_2H_6(g)) + 7/2\cdot (\Delta H_f^\circ(O_2(g)))) = -1561\ \text{kJ mol}^{-1}$

ENTHALPY (ΔH)

Write a chemical equation describing a) and c) and indicate the sign of ΔH

a) Melting ice:

b) what temperature does the process in a) occur naturally;

c) Freezing water:

d) what temperature does the process in a) occur naturally;

e) Is it possible to determine whether a process/change will occur naturally (thermodynamically favored) solely from the ΔH?

f) What other factor must be considered to determine whether a change is thermodynamically favored or not?

ENTROPY (ΔS)

A disordered pile of playing cards.

- High number of microstates of a system (more microstates is favored) Nature tends toward dispersal! Think about your room at the end of the week!
- think in terms of probability

ENTROPY (ΔS)

A disordered pile of playing cards.

- A thermodynamic quantity that is depended on the number of energetically equivalent possible arrangements of a system.
- think in terms of probability

ENTROPY (ΔS)

- Probable events have many ways to occur have high entropy;
- Improbable events have very few ways to occur have low entropy;
- Dispersal of position and energy
- Expanding gas

Statistical Thermodynamics

This is a way to use a particulate level view of matter to help understand the nature of entropy/disorder in terms of how the energy of the system is dispersed.

A microstate is like a snapshot of the system.

Statistical Thermodynamics

Lets consider a sample of an ideal gas in a container at a given temperature and pressure.

If we look at the distribution of particles in terms of position and energy we can get a better idea of the concept of a microstate.

A snapshot of the sample can be considered a microstate.

Statistical Thermodynamics

Boltzmann developed the relationship between entropy (S) and the number of microstates (W)

$$S = k \ln W$$

Statistical Thermodynamics

Boltzmann developed the relationship between entropy (S) and the number of microstates (W)

$$\Delta S = k \ln W_{final} - k \ln W_{initial}$$

$$\Delta S = k \ln (W_{final} / W_{initial})$$

For a change of condition ΔS is positive if the final condition has more microstates than the initial condition.

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

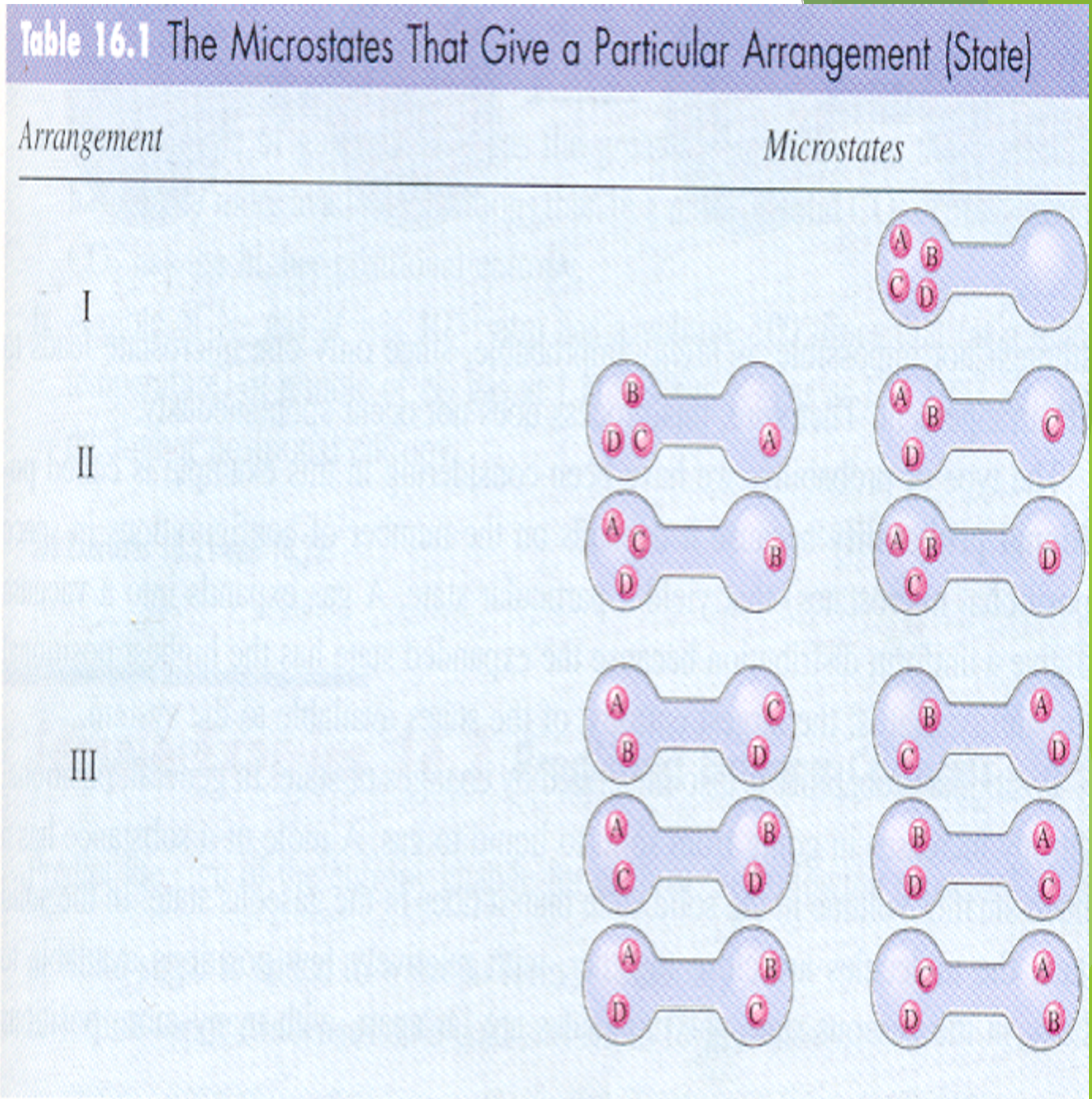

Table 16.1 The Microstates That Give a Particular Arrangement (State)

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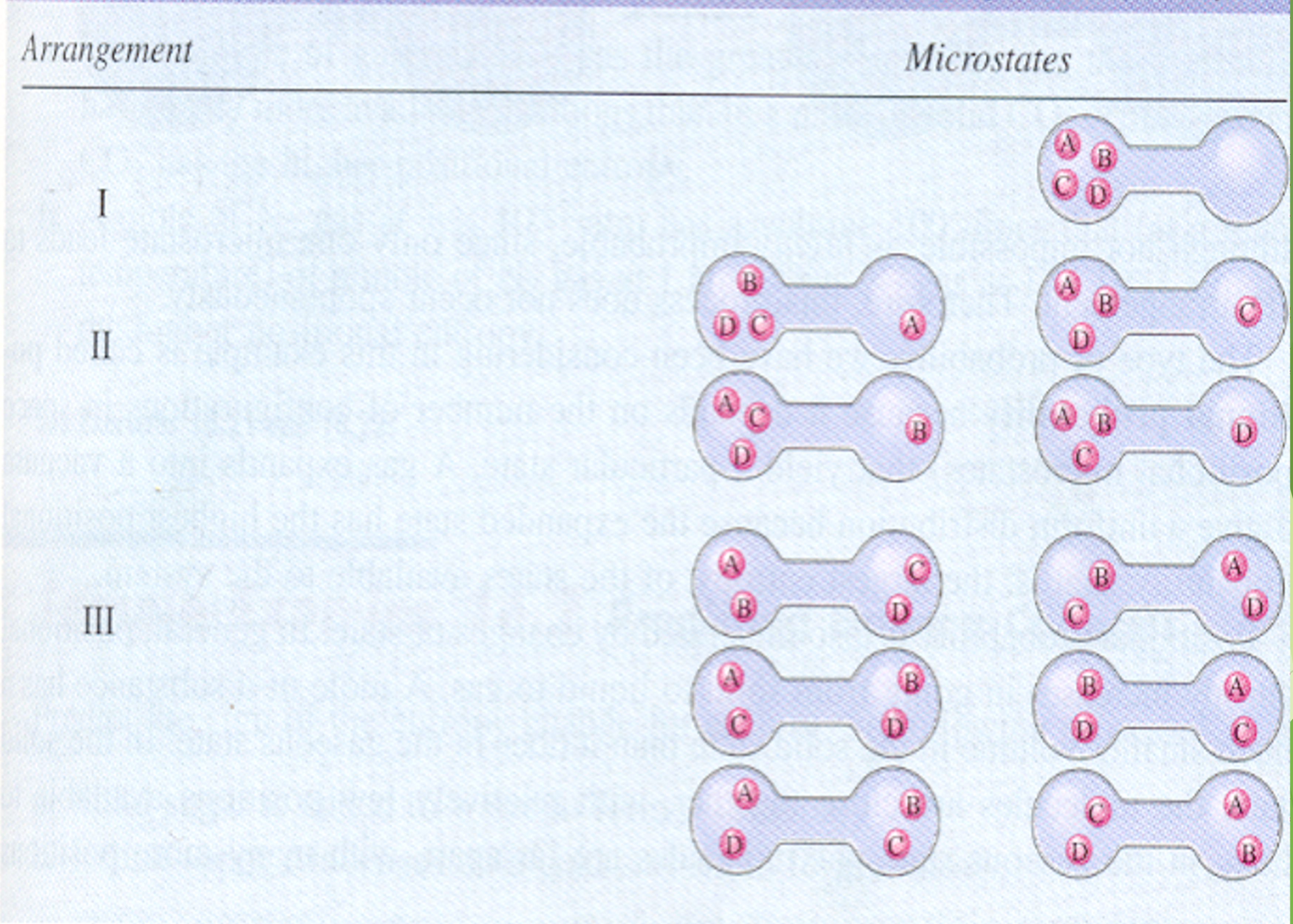
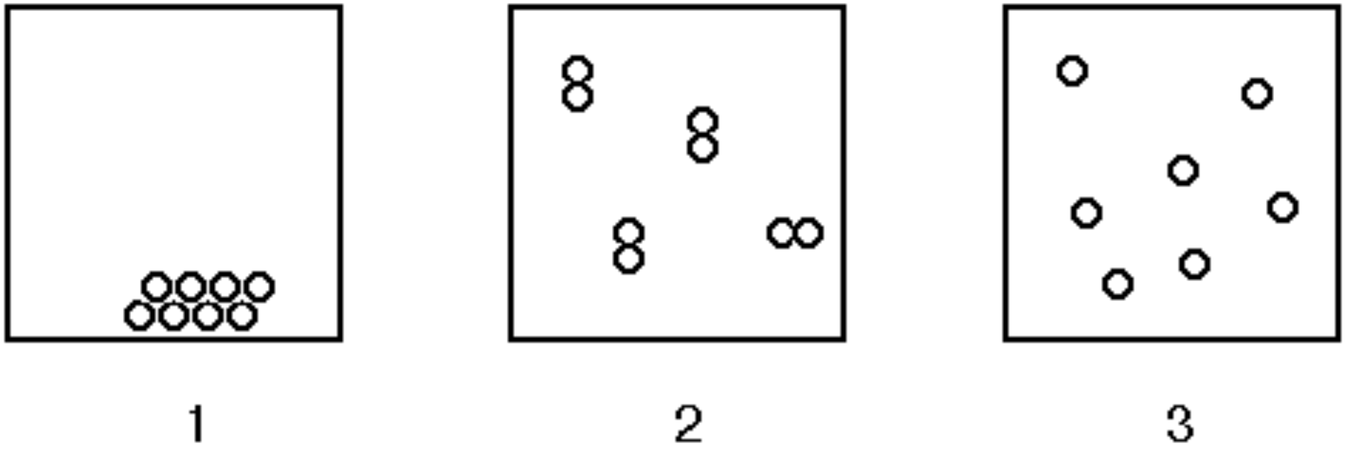


Predicting the entropy of a system based on physical evidence:



In which container are the particles more dispersed? Has the highest entropy?

In which are there more possible position, and energy microstates?

Predicting the entropy of a system based on physical evidence:

- Entropy is largest for gases, then liquids, and finally solids;
- Reactions increasing the number of moles of particles often increase entropy;
- Entropy generally increases with increasing molecular complexity (crystal structure: KCl vs $CaCl_2$) since there are more ***MOVING*** electrons!
- When a gas molecule escapes from a solvent, the entropy increases.

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.

Solution:

A: +ΔS

B: -ΔS

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

Answer:

a) the substance changes from a highly organized state to a more disorganized state.

ENTROPY
The Second Law of Thermodynamics

- 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.)

ENTROPY
The Third Law of Thermodynamics

- The entropy of a perfect crystal at 0 K 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 temperature higher than 0 K.

(Handy to know if you ever need to defend *why* ΔG_f°, ΔH_f° for elements = 0. . . BUT S° does not!)

Calculating Entropy from tables of standard values:

Just the same as calculating the enthalpy earlier.

BIG MAMMA, verse 2

$$\Delta S°_{rxn} = \Sigma\ S\ °_{(products)} - \Sigma\ S\ °_{(reactants)}$$

S is + when disorder increases (favored)

S is – when disorder decreases

Units are usually J/K· mol (not kJ ---tricky!)

Note: the entropy values for products and reactants are absolute, not Δ (change) in entropy!

Sample Problem B

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

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

Given the following absolute entropy 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

Solution:

Entropy change = -188.3 J/K · mol

SUMMARY

ENTROPY:

ΔS = + Products have more microstates (randomness, energy more dispersed) compared to reactants. (FAVORED CONDITION)

ΔS = - Reactants have more microstates (randomness, energy more dispersed) compared to products. (not favored)

PREDICTING ENTROPY CHANGES

a) $H_2O(s) \rightarrow H_2O(l)$

b) $2Mg(s) + O_2(g) \rightarrow 2MgO(s)$

c) $Ba(OH)_2 \cdot 8H_2O(s) + 2NH_4Cl(s) \rightarrow BaCl_2(aq) + 10H_2O(l) + 2NH_3(aq)$

d) $H_2(g) + 1/2O_2(g) \rightarrow H_2O(l)$

e) $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$

f) $Al(s) + 3/2Br_2(l) \rightarrow AlBr_3(s)$

PREDICTING ENTROPY CHANGES

Reaction	Sign ΔS
$H_2O(s) \rightarrow H_2O(l)$	+
$2Mg(s) + O_2(g) \rightarrow 2MgO(s)$	–
$Ba(OH)_2 \cdot 8H_2O(s) + 2NH_4Cl(s) \rightarrow BaCl_2(aq) + 10H_2O(l) + 2NH_3(aq)$	+
$H_2(g) + 1/2O_2(g) \rightarrow H_2O(l)$	–
$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$	~0
$Al(s) + 3/2Br_2(l) \rightarrow AlBr_3(s)$	–

Consider

$2\ H_2\ (g) + O_2\ (g) \rightarrow 2\ H_2O\ (g)$

ignite & rxn is fast!

$\Delta S_{system} = -88.9 J/K \cdot mol$

Entropy declines

(due mainly to 3 → 2 moles of gas!)

. . . to confirm we need to know entropy of surroundings

ΔH_{system} = - 483.6 kJ/mol

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

$$-\Delta H_{system} = \Delta H_{surroundings}$$

OR

$$-(-483.6\ kJ/mol) = +483.6\ kJ/mol$$

$\Delta S^\circ_{\text{surroundings}} =$

$$\frac{\Delta H^\circ_{\text{surroundings}}}{T} = \frac{+\ 483.6\ \text{kJ}}{298\ \text{K}}$$

$$= 1620\ \text{J/K}$$

Now we can find $\Delta S°_{\text{universe}}$

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

(-88.9 J/K) + (1620 J/K) = 1530 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.

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

$\Delta S^\circ_{\text{system}} + \Delta S^\circ_{\text{surroundings}} = \Delta S^\circ_{\text{universe}}$

$\Delta S^\circ_{\text{system}} - \Delta H^\circ_{\text{system}}/T = \Delta S^\circ_{\text{universe}}$

Multiply through by –T we get:

$-T\Delta S^\circ_{\text{system}} + \Delta H^\circ_{\text{system}} = -T\Delta S^\circ_{\text{universe}}$

Rename $-T\Delta S^\circ_{\text{universe}}$ as $\Delta G^\circ_{\text{system}}$

$-T\Delta S^\circ_{\text{system}} + \Delta H^\circ_{\text{system}} = \Delta G^\circ$

Now we can find $\Delta S°_{universe}$

$-T\Delta S°_{system} + \Delta H°_{system} = \Delta G°$

Rearrange;

$\Delta H°_{system} - T\Delta S°_{system} = \Delta G°$

So if we can calculate $\Delta H°$ and $\Delta S°$ for a reaction we can determine if the reaction is thermodynamically favored.

Check out the signs: $\Delta H°$ is – and $\Delta S°$ is + then $\Delta G°$ is –….. thermodynamically favored reaction.

PREDICTING ENTROPY CHANGES

Reaction	ΔH
$H_2O(s) \rightarrow H_2O(l)$	+
$2Mg(s) + O_2(g) \rightarrow 2MgO(s)$	–
$Ba(OH)_2{\cdot}8H_2O(s) + 2NH_4Cl(s) \rightarrow BaCl_2(aq) + 10H_2O(l) + 2NH_3(aq)$	+
$H_2(g) + 1/2O_2(g) \rightarrow H_2O(l)$	–
$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$	~0
$Al(s) + 3/2Br_2(l) \rightarrow AlBr_3(s)$	–

Predicting Free Energy CHANGES

Reaction	ΔH°(kJ/mol)	ΔS° (J/mol·K)
$H_2O(s) \rightarrow H_2O(l)$	+6.01	+39
$2Mg(s) + O_2(g) \rightarrow 2MgO(s)$	-1202	-213
$Ba(OH)_2 \cdot 8H_2O(s) + 2NH_4Cl(s) \rightarrow BaCl_2(aq) + 10H_2O(l) + 2NH_3(aq)$	+78	+428
$H_2(g) + 1/2O_2(g) \rightarrow H_2O(l)$	-286	-163
$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$	-803	-4
$Al(s) + 3/2Br_2(l) \rightarrow AlBr_3(s)$	-526	-72

FREE ENERGY

$H_2O(l) \rightarrow H_2O(g)$

$\Delta H^\circ = 44.0$ kJ/mol

$\Delta S^\circ = 119$ J/mol K = 0.119 kJ/mol K

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

$\Delta G^\circ = 44.0$ kJ/mol - 298 K (0.119 kJ/mol K) = 44.0 kJ/mol – 35.6 kJ/mol

$\Delta G^\circ = +8.5$ kJ/mol thermodynamically not favored

FREE ENERGY

$H_2O(l) \rightarrow H_2O(g)$

$\Delta H^\circ = 44.0$ kJ/mol

$\Delta S^\circ = 119$ J/mol K = 0.119 kJ/mol K

$0 = \Delta H^\circ - T\Delta S^\circ$

$0 = 44.0$ kJ/mol - T (0.119 kJ/mol K)

$T = -44{,}000 \text{ J mol}^{-1} / -119 \text{ J mol}^{-1} \text{ K}^{-1} =$ 370 K

FREE ENERGY

$H_2O(l) \rightarrow H_2O(g)$

$\Delta H^\circ = 44.0$ kJ/mol

$\Delta S^\circ = 119$ J/mol K = 0.119 kJ/mol K

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

$\Delta G^\circ = 44.0$ kJ/mol - 383K (0.119 kJ/mol K) = 44.0 kJ/mol – 45.6 kJ/mol

$\Delta G^\circ = -1.6$ kJ/mol thermodynamically favored

FREE ENERGY

- Calculation of Gibb's free energy is what **ultimately** decides whether a reaction is thermodynamically favored or not.
- ***NEGATIVE ΔG's are thermodynamically favored.***

ΔG can be calculated one of several ways:

Big Mamma, verse 3:

$$\Delta G^\circ_{rxn} = \Sigma\ m\Delta G_f^\circ\ _{(products)} - \Sigma\ n\Delta G_f^\circ\ _{(reactants)}$$

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

GRAND Daddy:

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

This puts together all information thus far!

<u>By far, one of the most beneficial equations to learn!</u>

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
$H_2O(l)$	-286 kJ/mol
$O_2(g)$	0 kJ/mol
$H_2O_2(l)$	-113.8 kJ/mol

Solution:

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

$\Delta G^\circ_{rxn} = \Sigma\ \Delta G^\circ_{(products)} - \Sigma\ \Delta G^\circ_{(reactants)}$

$\Delta G^\circ_{rxn} = 2\Delta G^\circ\left(H_2O_2(l)\right) - [2\Delta G^\circ(H_2O(l)) + \Delta G^\circ(O_2(g)]$

$\Delta G^\circ_{rxn} = 2*(-114\ kJ/mol) - [2*(-286\ kJ/mol + 0]$

$\Delta G^\circ_{rxn} = 344\ kJ/mol$

Exercise 9 (GRAND Daddy: $\Delta G = \Delta H - T\Delta S$)

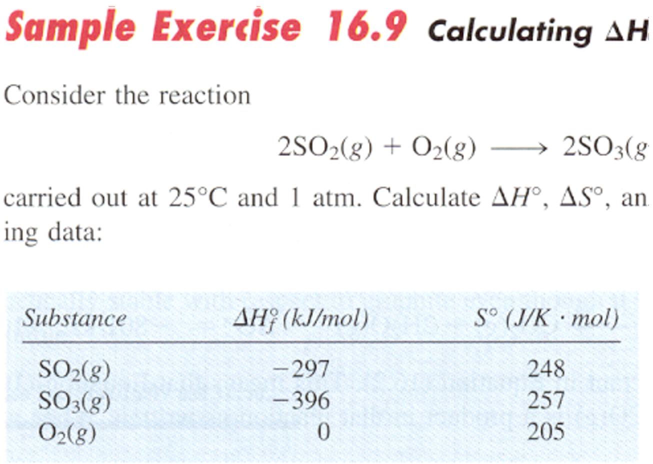
Calculating $\Delta H°$, $\Delta S°$, and $\Delta G°$

Consider the reaction:

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

carried out at 25°C and 1 atm.

Calculate ΔH°, ΔS°, and ΔG° using the following data:



Sample Exercise 16.9 **Calculating ΔH**

Consider the reaction

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

carried out at 25°C and 1 atm. Calculate $\Delta H°$, $\Delta S°$, an
ing data:

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

Solution:

ΔH° = -198 kJ/mol

ΔS° = -187 J/K · mol

ΔG° = -142 kJ/mol

Exercise 10 (Hess's law of summation) Calculating ΔG°

Using the following data (at 25°C):

$C_{diamond}(s)+O_2(g)\rightarrow CO_2(g)$ ΔG°= -397 kJ/mol

$C_{graphite}(s)+O_2(g)\rightarrow CO_2(g)$ ΔG°= -394 kJ/mol

Calculate ΔG° for the reaction:

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

Solution:

$\Delta G° = -3$ kJ/mol

SUMMARY OF FREE ENERGY:

ΔG = + thermodynamically not favored

ΔG = - thermodynamically favored

Conditions of ∆G:

∆H	∆S	Result
neg	pos	thermodynamically favored at all T
pos	pos	thermodynamically favored at high T
neg	neg	thermodynamically favored at low T
pos	neg	thermodynamically not favored, ever