From Thermo*chemistry* to Thermo*dynamics*

The study of what drives chemical reactions.

What really makes a reaction happen?

So where have we been, where are we now? Where are we going?

- Chemical Reactions
  - ✓ What is reacting, what is produced?
- Stoichiometry
  - ✓ How much of each reactant do we need?
  - ✓ How much of each product is produced?
- Equilibrium
  - ✓ To what extent does a reaction proceed before “stopping?”
- Thermodynamics
  - ✓ Under the stated conditions does a reaction move forward or reverse? Is a reaction spontaneous?
  - ✓ How do energy and entropy affect the spontaneity?
- Kinetics
  - ✓ How fast does a reaction happen?
  - ✓ What factors affect that rate?

Spontaneity and Kinetics and Reaction Direction

- Spontaneity is unrelated to the speed of a reaction - It’s *kinetics* that tells us about the rate of a reaction.
  - ✓ Some spontaneous processes may be extremely slow.
  - ✓ Some may be fast.
- Spontaneity simply tells us the direction in which a reaction proceeds, not the speed.

The Common-Sense Law

The Second Law of Thermodynamics

- The universe has a preference towards lower energy and matter more dispersed.
  - ✓ Hot objects transfer their heat to cooler surroundings, *but* never does heat move from cool objects to hot ones.
  - ✓ Exothermic reactions like combustions seem to be very favorable.
  - ✓ Marbles will scatter, *but* not roll back in the bag.
  - ✓ Jigsaw puzzles disassemble easily, *but* shaking the box never results in reassembly.
- In a sense, the universe is trying to be a lazy slob.

What drives reactions, and determines spontaneity?

Dispersal of energy AND matter

high **Entropy**

and

low **Energy**

processes that move toward higher entropy and lower energy are thermodynamically favorable

So just what is entropy? ⟶

Entropy

We can loosely describe entropy to be a measure of the disorder of a substance

Let's make some comparisons to help us learn about trying to predict differences in entropy of matter.

Which has the *least* amount of entropy?

1. solid
2. liquid
3. gas
4. not enough information to determine

Which has the least amount of entropy?

1. solid
   - phase is an important factor in determining entropy
2. liquid
3. gas
4. not really enough information to determine

Which has least entropy at room conditions

1. 1 mole of gold
2. 1 mole of mercury
3. equal amounts of entropy since there is 1 mole of each substance
4. not enough information to determine

Which has least entropy at room conditions

1. 1 mole of gold,
   - since gold is solid, yet the mercury would be liquid at room temp.
   - Yes, AP expects you to know the phase of elements at room conditions.
   - Again, phase is a very important factor when deciding on entropy
2. 1 mole of mercury
3. equal amounts of entropy since there is 1 mole of each substance
4. not enough information to determine

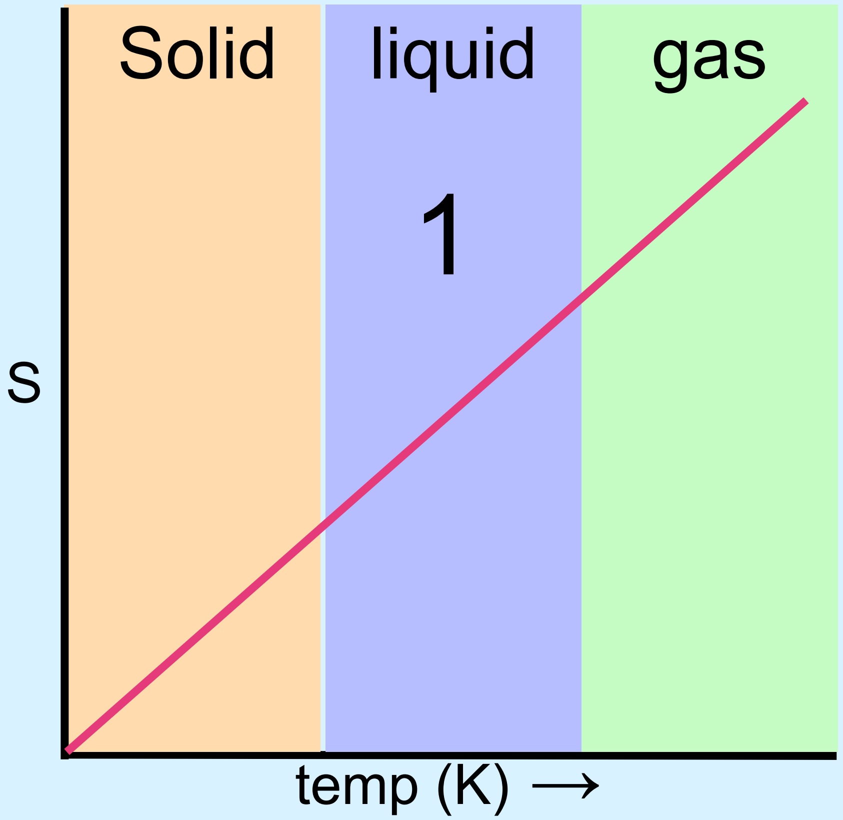
Which has more entropy?

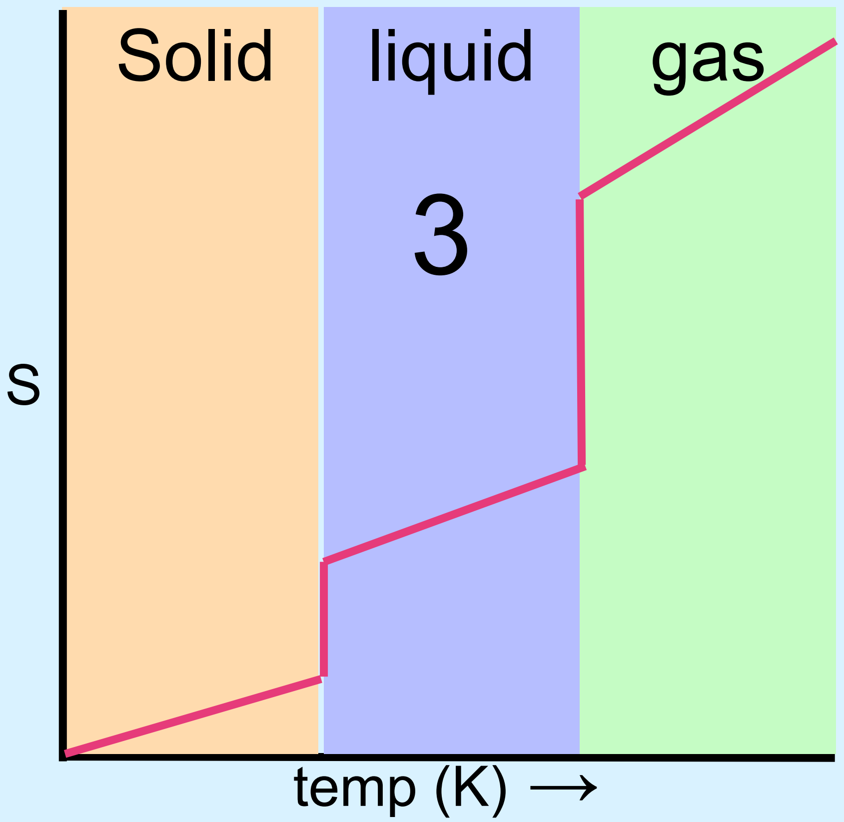
1. 1 mol $He_{(g)}$ at 0ºC in 1 L
2. 1 mol $He_{(g)}$ at 10 K in 1 L
3. not enough information to determine
4. 1 and 2 have the same entropy

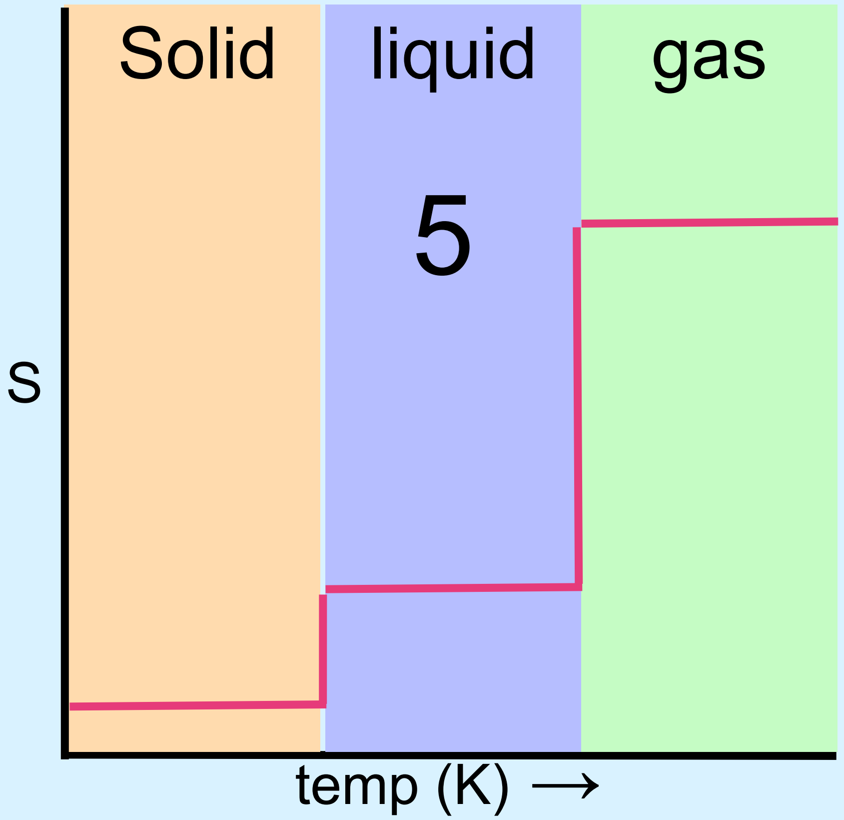
Which has more entropy?

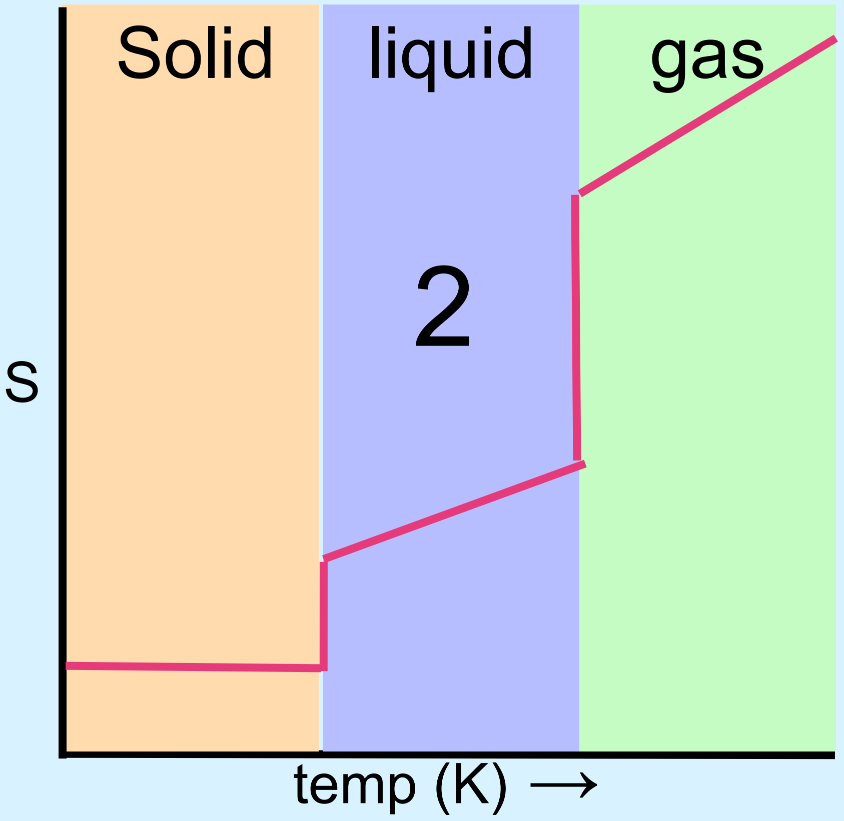
1. He at 0ºC
   - All other parameters being equal, higher temp, means higher entropy
2. He at 10 K
3. not enough information to determine
4. 1 and 2 have the same entropy

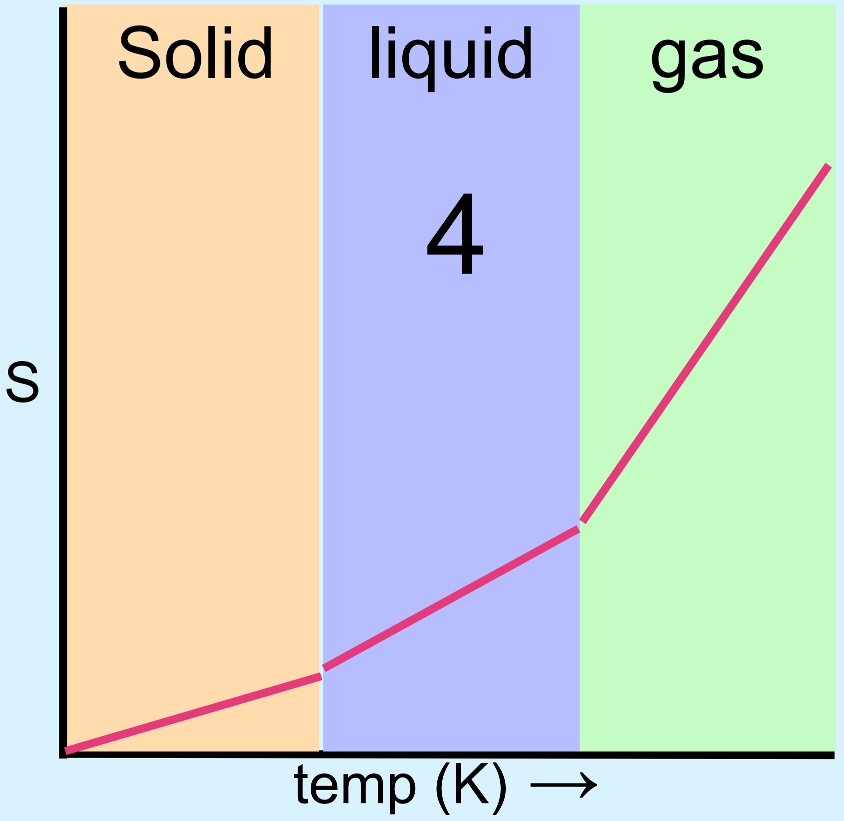
Which graph below might best represent entropy (S) changes as temperature increases

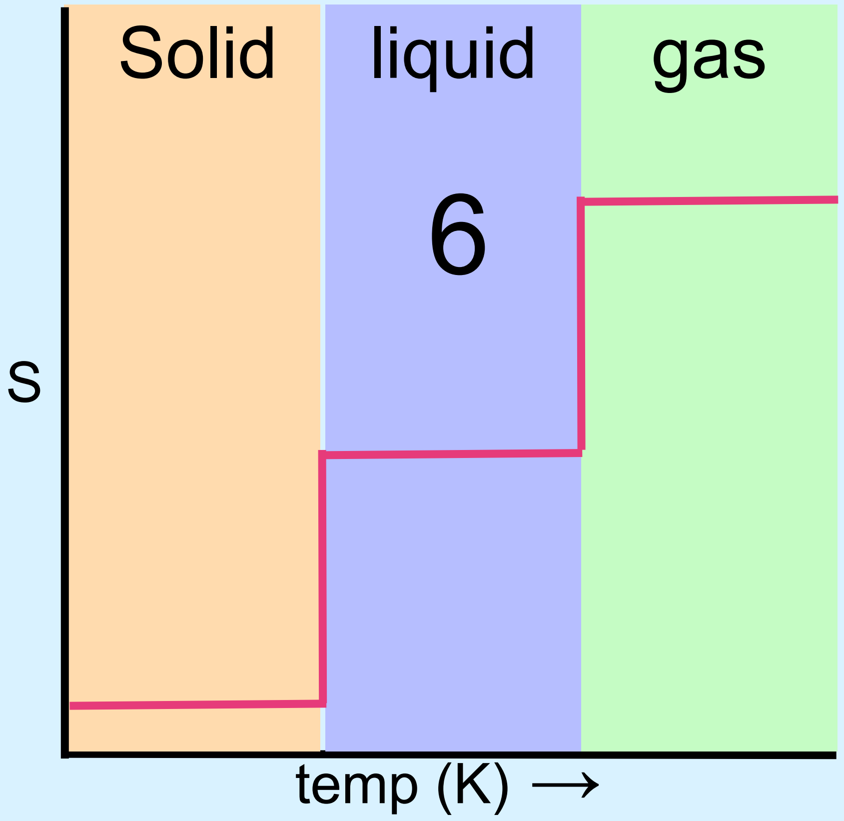






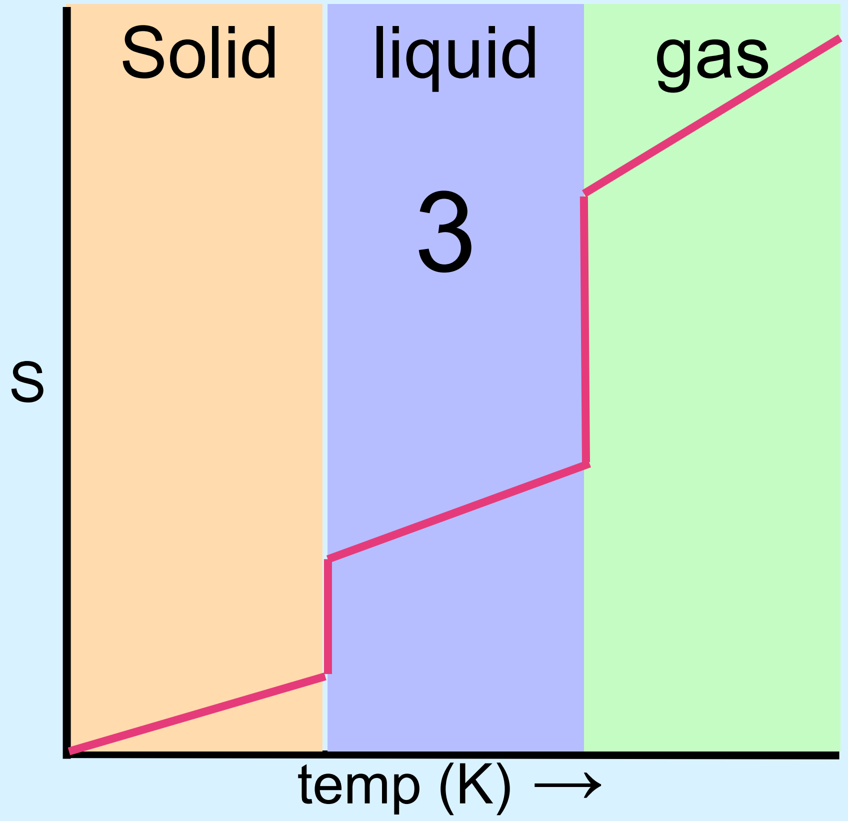


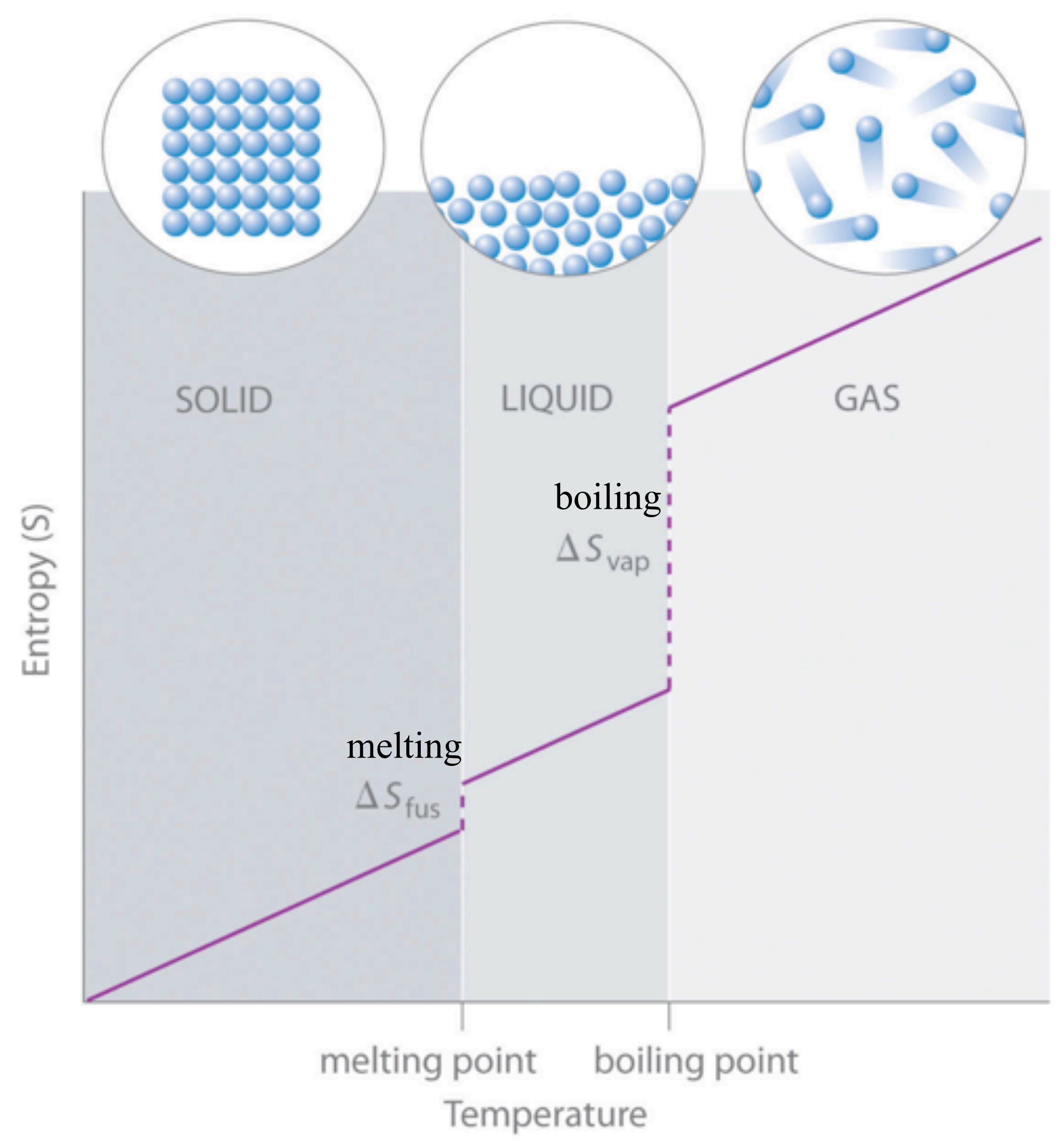




Which graph below might best represent entropy changes as temperature increases

- #3
- Note the larger entropy change for the L-G phase change





Which gas has more entropy?

1. 1 mol NO
2. 1 mol NO_2
3. they have the same entropy
4. not enough information to determine
5. I have absolutely no idea how I would even venture a guess.

These gases are at the same T, P, V conditions.

Which gas has more entropy?

These gases are
at the same T, P, V
conditions.

1. NO
2. NO_2

- All else being the same, larger molecules have higher entropy. There are more confirmations and more ways to distribute energy.
- Let's look them up in the thermodynamic sheets.

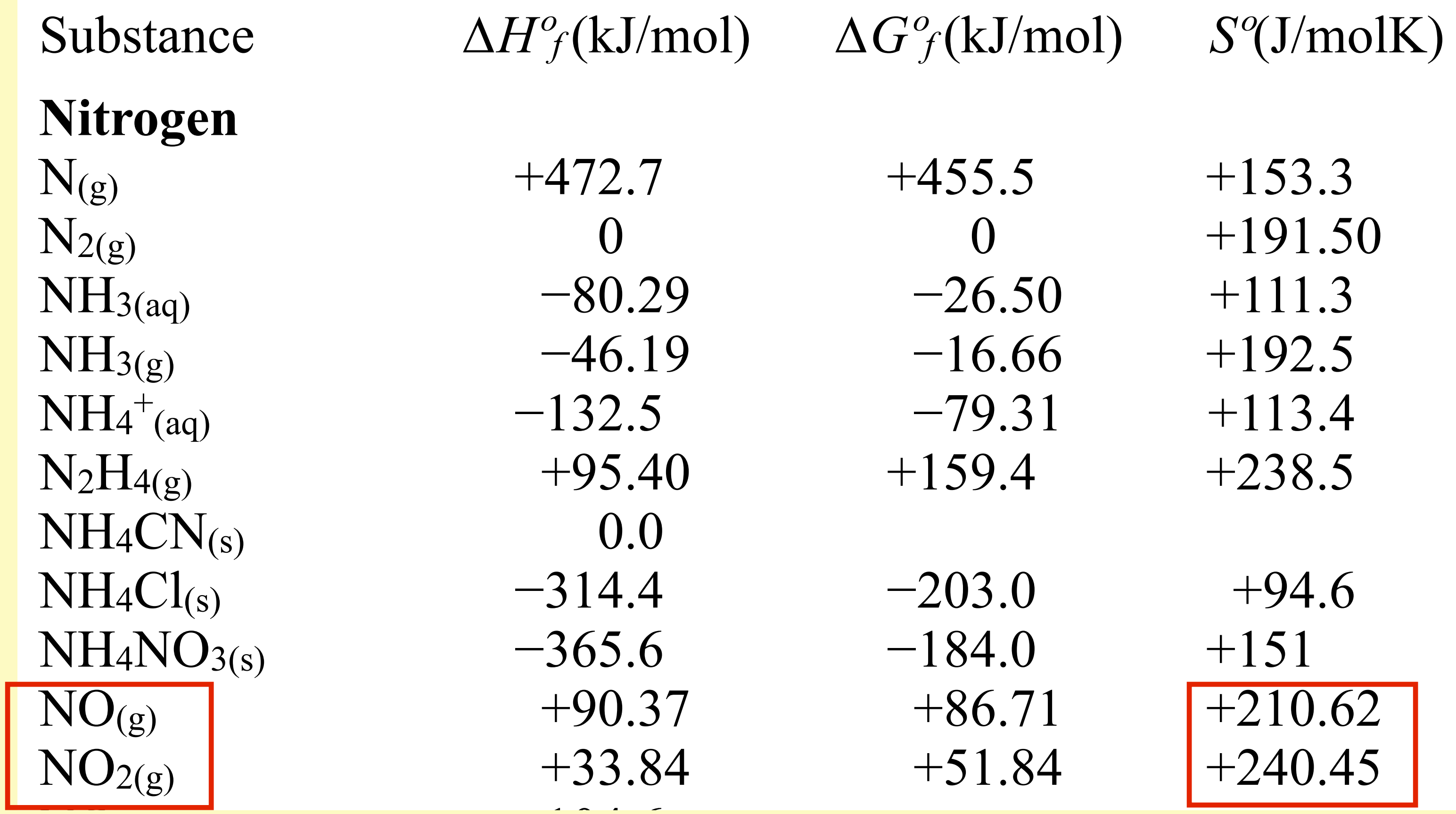
3. they have the same entropy
4. not enough information to determine
5. I have absolutely no idea how I would even venture a guess.

Looking up absolute entropy on the thermodynamic sheets.

These gases are at the same T, P, V conditions.

1. NO (211 J/molK)
2. NO_2 (240 J/molK)

- All else being the same, larger molecules have higher entropy.There are more confirmations and more ways to distribute energy.



Substance	ΔH^o_f(kJ/mol)	ΔG^o_f(kJ/mol)	S^o(J/molK)
Nitrogen			
$N_{(g)}$	+472.7	+455.5	+153.3
$N_{2(g)}$	0	0	+191.50
$NH_{3(aq)}$	−80.29	−26.50	+111.3
$NH_{3(g)}$	−46.19	−16.66	+192.5
$NH_4^+{}_{(aq)}$	−132.5	−79.31	+113.4
$N_2H_{4(g)}$	+95.40	+159.4	+238.5
$NH_4CN_{(s)}$	0.0		
$NH_4Cl_{(s)}$	−314.4	−203.0	+94.6
$NH_4NO_{3(s)}$	−365.6	−184.0	+151
$NO_{(g)}$	+90.37	+86.71	+210.62
$NO_{2(g)}$	+33.84	+51.84	+240.45

Which has more entropy?

1. 10 ml of 1 M NaCl
2. 10 ml of 2 M NaCl
3. 1 and 2 have the same entropy since they both represent the same ionic compound in solution.

Which has more entropy?

1. 10 ml of 1 M NaCl
2. 10 ml of 2 M NaCl

- All other parameters being equal, higher concentration will have more entropy since there are more molecules present creating more positional posibilities.

3. 1 and 2 have the same entropy since they both represent the same molecule.

Which has more entropy?

1. 1 mole $HF_{(g)}$ at 25ºC, 1 atm
2. 1 mole $HCl_{(g)}$ at 25ºC, 1 atm
3. not enough information to determine
4. 1 and 2 have the same entropy

Which has more entropy?

1. 1 mole $HF_{(g)}$ at 25ºC, 1 atm
2. 1 mole $HCl_{(g)}$ at 25ºC, 1 atm
   - Other parameters being equal, larger atoms will have more entropy.
   - Let's look them up on the Thermodynamic sheets.
3. not enough information to determine
4. 1 and 2 have the same entropy

Using the Thermodynamic Tables

1. 1 mole $HF_{(g)}$ at 25ºC, 1 atm
   - (174 J/mol K)
2. 1 mole $HCl_{(g)}$ at 25ºC, 1 atm
   - (187 J/mol K)
   - Likely, the more entropy is due to Cl's larger electron cloud.
   - Not likely, that AP would ask you to estimate which of these has more entropy, though it is worth noting.
   - Other parameters being equal, larger atoms will have more entropy.

Which has more entropy?

at the same temp, same volume

1. two moles of $NO_{2(g)}$
2. one mole of $N_2O_{4(g)}$

- hmmmm this is a tough one!

3. the same
4. not enough information to determine

Which has more entropy?

at the same temp, same volume

1. two moles of NO_2
2. one mole of N_2O_4

- hmmmm this is a tough one!
- Lets look it up on the Thermo Sheets

3. the same
4. not enough information to determine

Which has more entropy?

at the same temp, same volume

1. two moles of NO_2 240.45 J/molK
2. one mole of N_2O_4 304.3 J/molK

- hmmmm this is a tough one!

3. the same
4. not enough information to determine

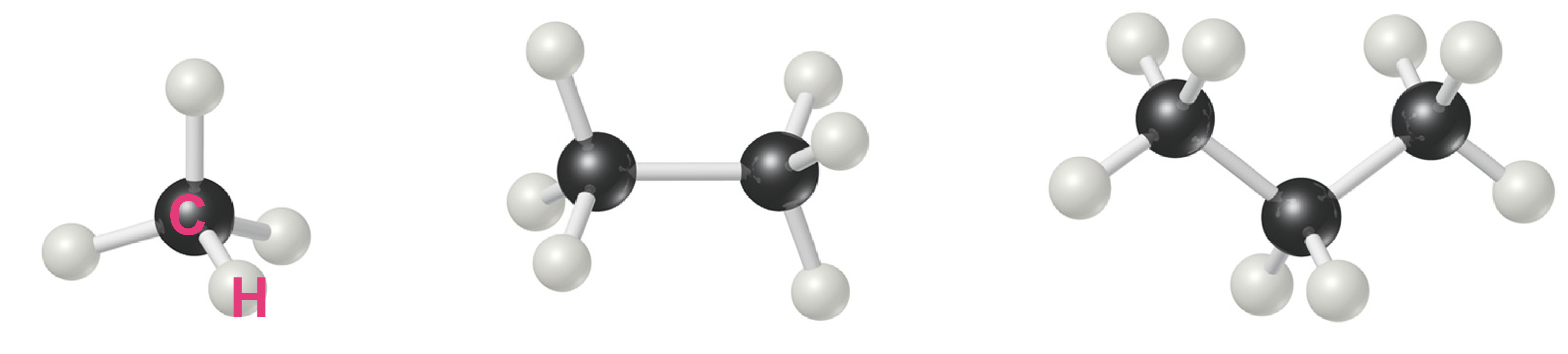
Which has more entropy?

at the same temp, same volume

1. two moles of NO_2 2(240.45 J/molK)
   - since these molecules are not tied together with a bond, they have more “degrees of freedom” or positional possibilities.
   - more molecules means more entropy.
2. one mole of N_2O_4 (304.3 J/molK)
3. the same
4. not enough information to determine

Which has the most entropy?

All molecules at the same temperature.

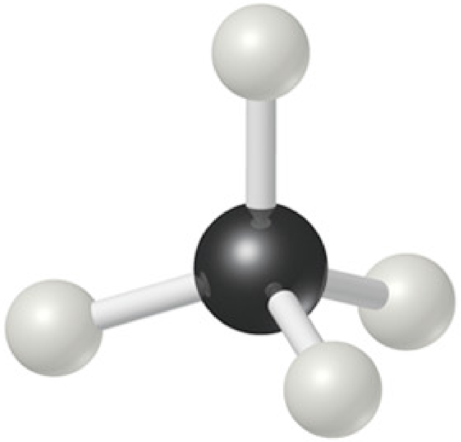


1 2 3

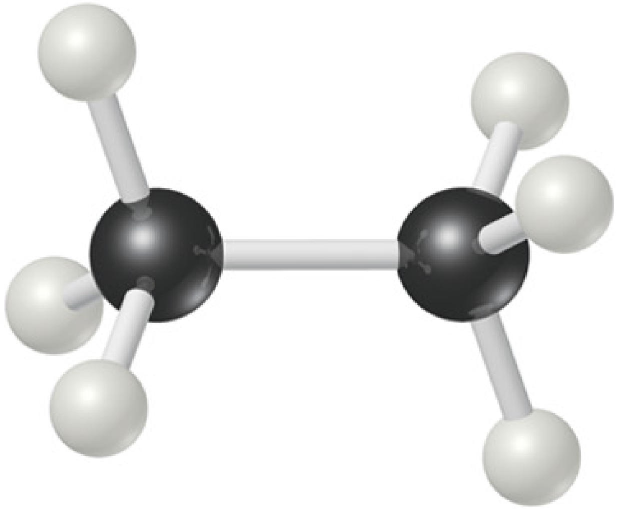
And can you name these three molecules?

Which has the most entropy?

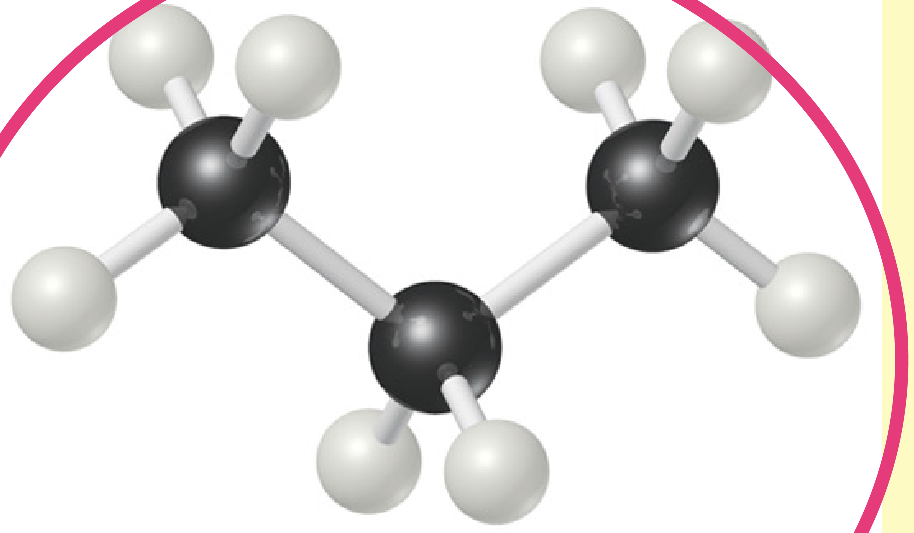
- Propane is larger and thus has more entropy than smaller molecules.



Methane, CH_4
$S^\circ = 186.3\ \mathrm{J\ mol^{-1}\ K^{-1}}$



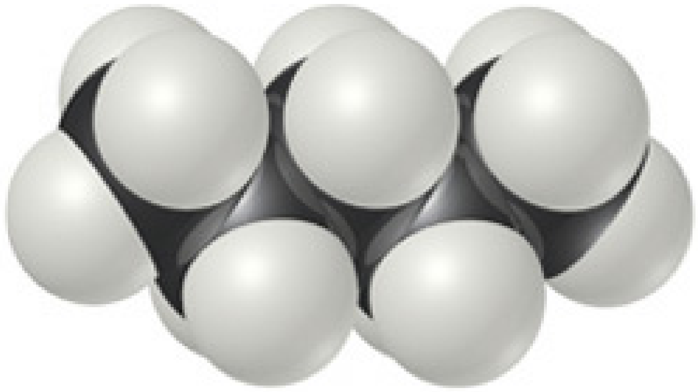
Ethane, C_2H_6
$S^\circ = 229.6\ \mathrm{J\ mol^{-1}\ K^{-1}}$



Propane, C_3H_8
$S^\circ = 270.3\ \mathrm{J\ mol^{-1}\ K^{-1}}$

Which has the most entropy?

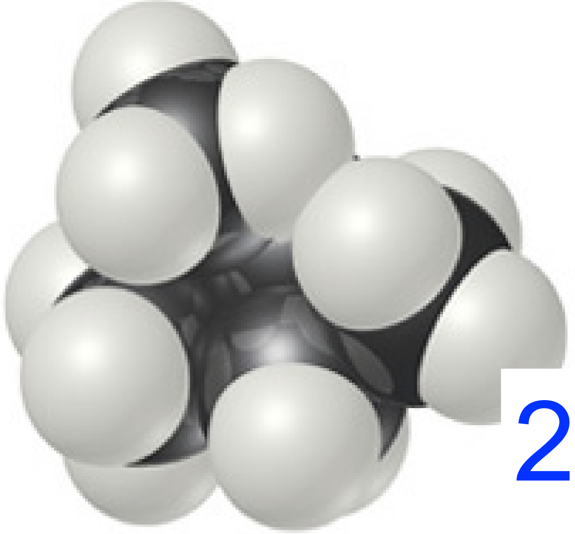
Isomers: Same chemical formula but different structures



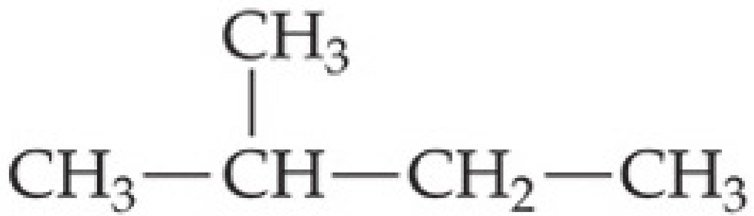
1

$CH_3CH_2CH_2CH_2CH_3$

C_5H_{12}

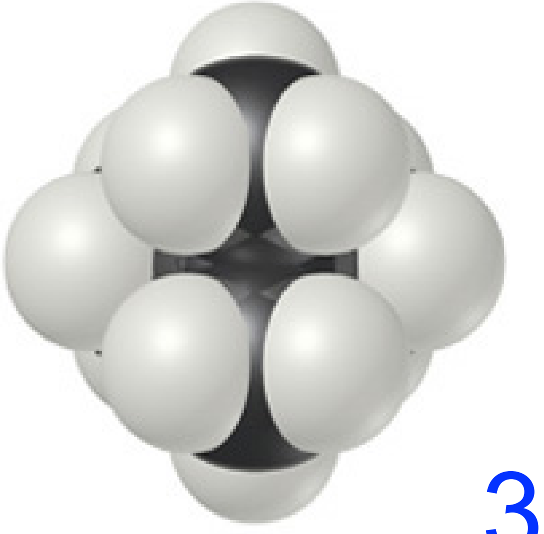


2

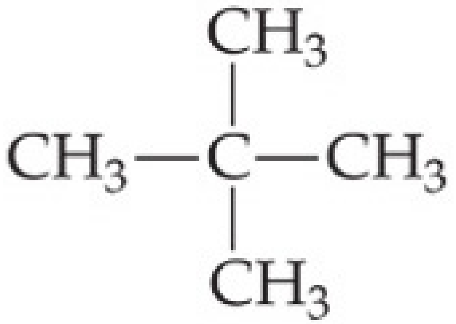


$$\begin{array}{c}\quad CH_3 \\ \quad | \\ CH_3-CH-CH_2-CH_3\end{array}$$

C_5H_{12}



3



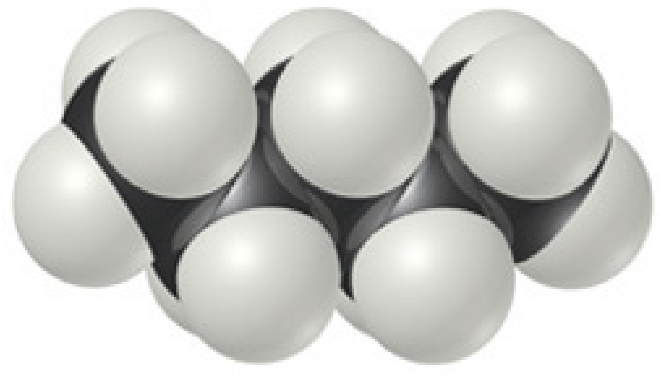
$$\begin{array}{c}CH_3 \\ | \\ CH_3-C-CH_3 \\ | \\ CH_3\end{array}$$

C_5H_{12}

#4 If more than one structure has the same entropy.

Which has the most entropy?

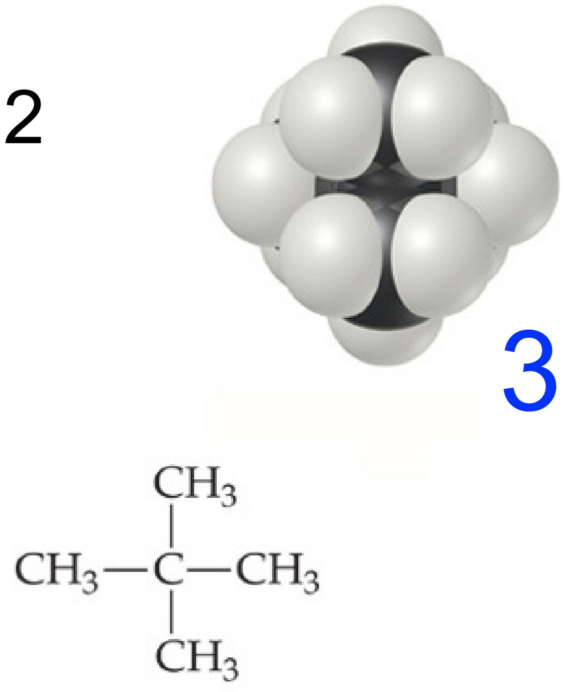
- All other factors equal, straight chain molecules have more “degrees of freedom” than branched chain molecules.
- Straight chains are more “floppy.”
- What is the name of molecule #1?



1

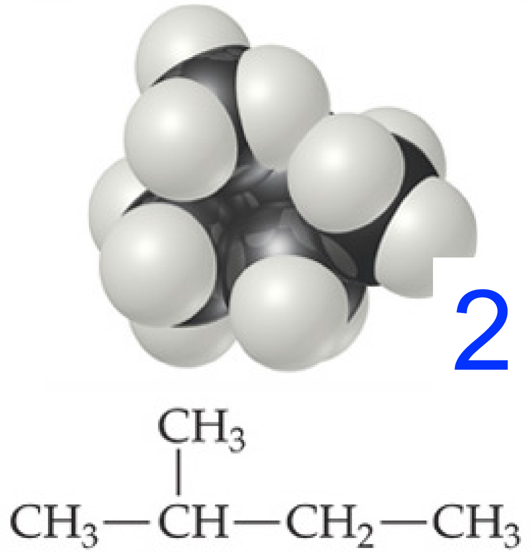
$CH_3CH_2CH_2CH_2CH_3$

C_5H_{12}



3

$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$$

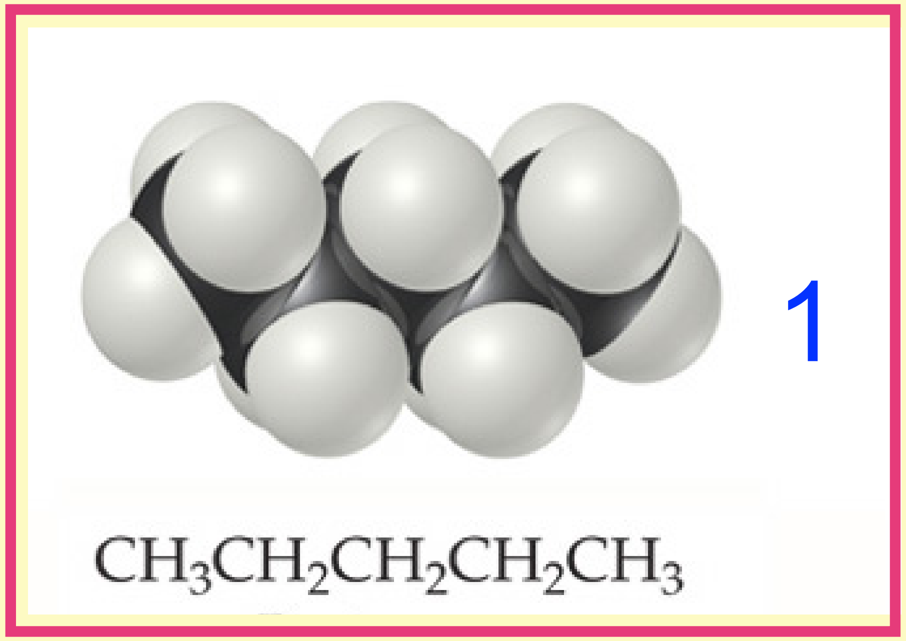


2

$$CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_2-CH_3$$

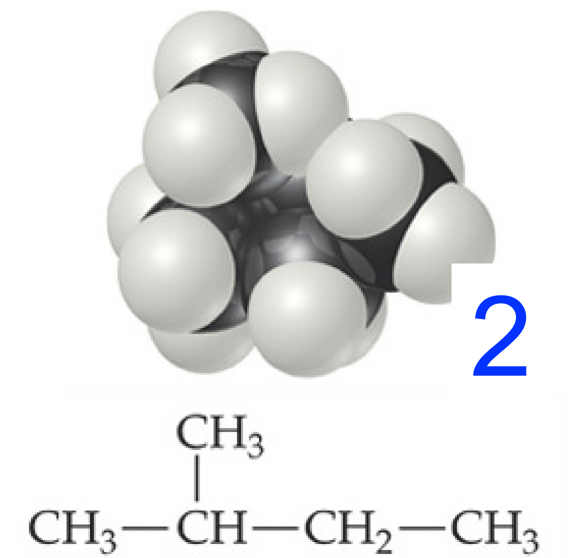
Which has the most entropy?

- All other factors equal, straight chain molecules have more "degrees of freedom" than branched chain molecules.
- Straight chains are more "floppy."
- What is the name of molecule #1?
- Pentane

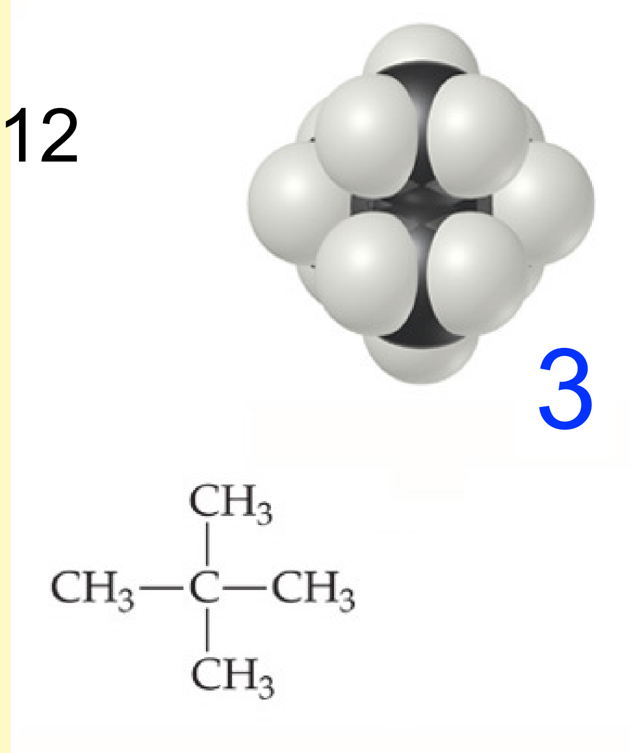


$CH_3CH_2CH_2CH_2CH_3$

C_5H_{12}



$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}H}-CH_2-CH_3$$



$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-CH_3$$

When predicting the entropy of one substance to another, consider

- ★ Phase
  - gases have significantly more entropy than liquids which have more entropy than solids
- ★ Number of molecules
  - First consider the number of molecules in the gas phase, before considering any other molecules
  - Next consider total number of molecules
  - More molecules have more positional possibilities, which means more entropy
- temperature
  - higher temperature causes greater entropy
- molecule size
  - significantly larger molecules have more entropy because they have more bending and folding options
- molecule shape
  - long, straight chained molecules have more entropy than branched molecules
- larger atoms
  - for similar molecules, the one that contains larger atoms with larger electron cloud, will have more entropy

It is not likely that AP will ask you to compare the entropy of two different substances. They generally ask about the change during a chemical reaction.

When predicting the entropy of a chemical reaction, consider

★Phase

- gases have significantly more entropy than liquids which have more entropy than solids

★Number of molecules

- First consider the number of molecules in the gas phase, before considering any other molecules
- Next consider total number of molecules
- More molecules have more positional possibilities, which means more entropy

If there are conflicting conditions, consider the change in the number of gas molecules as the determining factor.

Select the process(es) below in which entropy increases, $\Delta S = +$

Predict without using your thermo sheets

1. $CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$
2. $2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)}$
3. $H_2O_{(g)} \rightarrow H_2O_{(L)}$
4. $Fe_3O_{4(s)} + 4H_{2(g)} \rightarrow 3Fe_{(s)} + 4H_2O_{(g)}$

Select the processes below in which entropy increases.

1. $CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$
- solid reactant to 1 mol gas product

2. $2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)}$
   - 3 mol gas reactant to 2 mol gas product

3. $H_2O_{(g)} \rightarrow H_2O_{(L)}$
   - 1 mol gas reactant to only liquid product

4. $Fe_3O_{4(s)} + 4H_{2(g)} \rightarrow 3Fe_{(s)} + 4H_2O_{(g)}$
- 4 mol gas reactant to 4 mol gas product, but total 5 mol reactant to 7 mol product

Use your thermodynamic table to calculate ΔSº for $CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$

- Report your answer to the nearest whole number.

$$\boxed{\Delta S_{rxn} = \Sigma n S^{o}_{\text{Products}} - \Sigma n S^{o}_{\text{Reactants}}}$$

Use your thermodynamic table to calculate ΔS^o for $CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$

- [(+39.75 J/molK + (+213.6 J/molK)] − (+92.88 J/molK) = **+160.47 J/molK**
- A positive value as you would predict because of the formation of a gas.

Use your thermodynamic table to calculate ΔS^{o} for $2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)}$

- Report your answer to the nearest whole number.

Use your thermodynamic table to calculate ΔSº for $2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)}$

- 2(+256.2 J/molK) - [2(+248.5 J/molK + (+205.0 J/molK)]
- = -189.6 J/molK
- A negative value as you would predict because of the change of 3 moles of gas into only 2 moles of gas.

Use your thermodynamic table to calculate ΔSº for

$$H_2O_{(g)} \leftrightharpoons H_2O_{(L)}$$

- Report your answer to the nearest whole number.

Use your thermodynamic table to calculate ΔSº for $H_2O_{(g)} \leftrightharpoons H_2O_{(L)}$

- (+69.91 J/molK) + (+188.83 J/molK) = −118.92 J/molK
- A negative value as you would predict because of the phase change from a gas to a liquid.

Use your thermodynamic table to calculate ΔSº for

$Fe_3O_{4(s)} + 4H_{2(g)} \rightarrow 3Fe_{(s)} + 4H_2O_{(g)}$

- Report your answer to the nearest whole number.

Use your thermodynamic table to calculate ΔSº for $Fe_3O_{4(s)} + 4H_{2(g)} \longrightarrow 3Fe_{(s)} + 4H_2O_{(g)}$

[3(+27.15 J/molK + 4(+188.83 J/molK)] − [(+146.4 J/molK) + 4(+130.58 J/molK)]

- = +168 J/molK
- A positive value as you would predict because of the change of 5 moles of reactant into only 7 moles of product, while moles of gas is same on both side.

Select the process(es) below in which entropy increases, $\Delta S = +$

Predict without using your thermo sheets

1. $2O_{3(g)} \rightarrow 3O_{2(g)}$
2. $2CH_{4(g)} \rightarrow C_2H_{6(g)} + H_{2(g)}$
3. $NaCl_{(s)} \rightarrow Na^{+}_{(aq)} + Cl^{-}_{(aq)}$

Select the processes below in which entropy increases.

Let's take a closer look at each one of these examples on the next slides

1. $2O_{3(g)} \leftrightarrows 3O_{2(g)}$
2. $2CH_{4(g)} \rightarrow C_2H_{6(g)} + H_{2(g)}$
   - It would be highly unlikely that you would be asked to distinguish something like this as it is a VERY tough decision as demonstrated by the following slides showing that there is very small entropy decrease.
3. $NaCl_{(s)} \rightarrow Na^{+}_{(aq)} + Cl^{-}_{(aq)}$
   - Unless there is some other info in the problem indicating otherwise, you can assume ΔS is positive for dissolution.

Use your thermodynamic table to calculate ΔS^o for $2O_{3(g)} \rightarrow 3O_{2(g)}$

- Report your answer to the nearest whole number.

Use your thermodynamic table to calculate ΔS^o for $2O_{3(g)} \longrightarrow 3O_{2(g)}$

- 3(+205 J/molK) − 2(+237.6 J/molK)] = +139.8 J/molK
- This is a *positive* entropy change which makes sense since
  - gas on both sides
  - # molecules increases during the reaction

Use your thermodynamic table to calculate ΔS° for
$2CH_{4(g)} \rightarrow C_2H_{6(g)} + H_{2(g)}$

- Report your answer to the nearest whole number.

Use your thermodynamic table to calculate ΔSº for $2CH_{4(g)} \rightarrow C_2H_{6(g)} + H_{2(g)}$

- $[(+229.5\ \text{J/molK}) + (+130.58\ \text{J/molK})] - 2(+186.3\ \text{J/molK}) =$
  $-12.52\ \text{J/molK}$
- This is a *very* small entropy change which makes sense since
  - gas on both sides
  - same # molecules on both sides
  - It is possible that the very limited positional possibilities for the tiny H_2 molecule, contribute to the decrease in entropy.

Use your thermodynamic table to calculate ΔSº for

$NaCl_{(s)} \rightarrow Na^{+}_{(aq)} + Cl^{-}_{(aq)}$

- Report your answer to the nearest whole number.

Use your thermodynamic table to calculate ΔSº for

$NaCl_{(s)} \rightarrow Na^+_{(aq)} + Cl^-_{(aq)}$ (or $NaCl_{(aq)}$)

- [(+59.0 J/molK) + (56.5 J/molK)] − (+72.33 J/molK) = +43 J/molK
- This is a *positive ΔS, thermodynamically favorable, as you would expect from a salt breaking apart into its ions.*

Use your thermodynamic table to calculate ΔSº for

$MgCl_{2(s)} \rightarrow Mg^{2+}{}_{(aq)} + 2Cl^{-}{}_{(aq)}$

- Report your answer to the nearest whole number.

Use your thermodynamic table to calculate ΔSº for

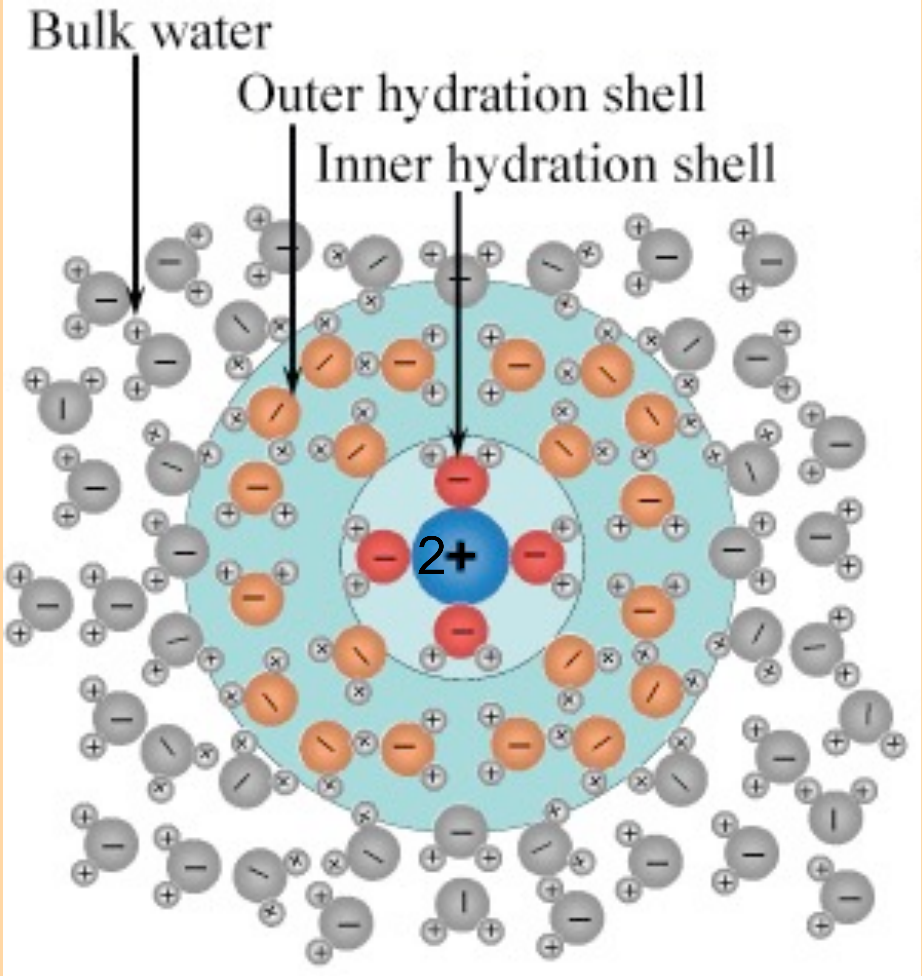
$MgCl_{2(s)} \rightarrow Mg^{2+}_{(aq)} + 2Cl^{-}_{(aq)}$

- [(−137 J/molK) + 2(+56.1 J/molK)] − (+89.6 J/molK) = −114.4 J/molK
- This is a *negative* Δ*S, thermodynamically unfavorable, Whaaaat!!!???*
- *What is going on here???*

When some salts dissolve, ΔS° for the process is actually negative

$$MgCl_{2(s)} \rightarrow Mg^{2+}_{(aq)} + 2Cl^{-}_{(aq)}$$

- The entropy of the process considers both the water and the salt.
- While the salt certainly becomes more disordered, the water actually becomes more ordered.
- The water molecules arrange around the ions. Tis is called a hydration shell and it makes the water part of the system decreases in entropy.
- For this particular salt, the entropy of the water decreases more than the entropy of the salt increases.
- You will NOT be expected to know for which salts this occurs. But be alert for a question giving you information that should led you to this conclusion.



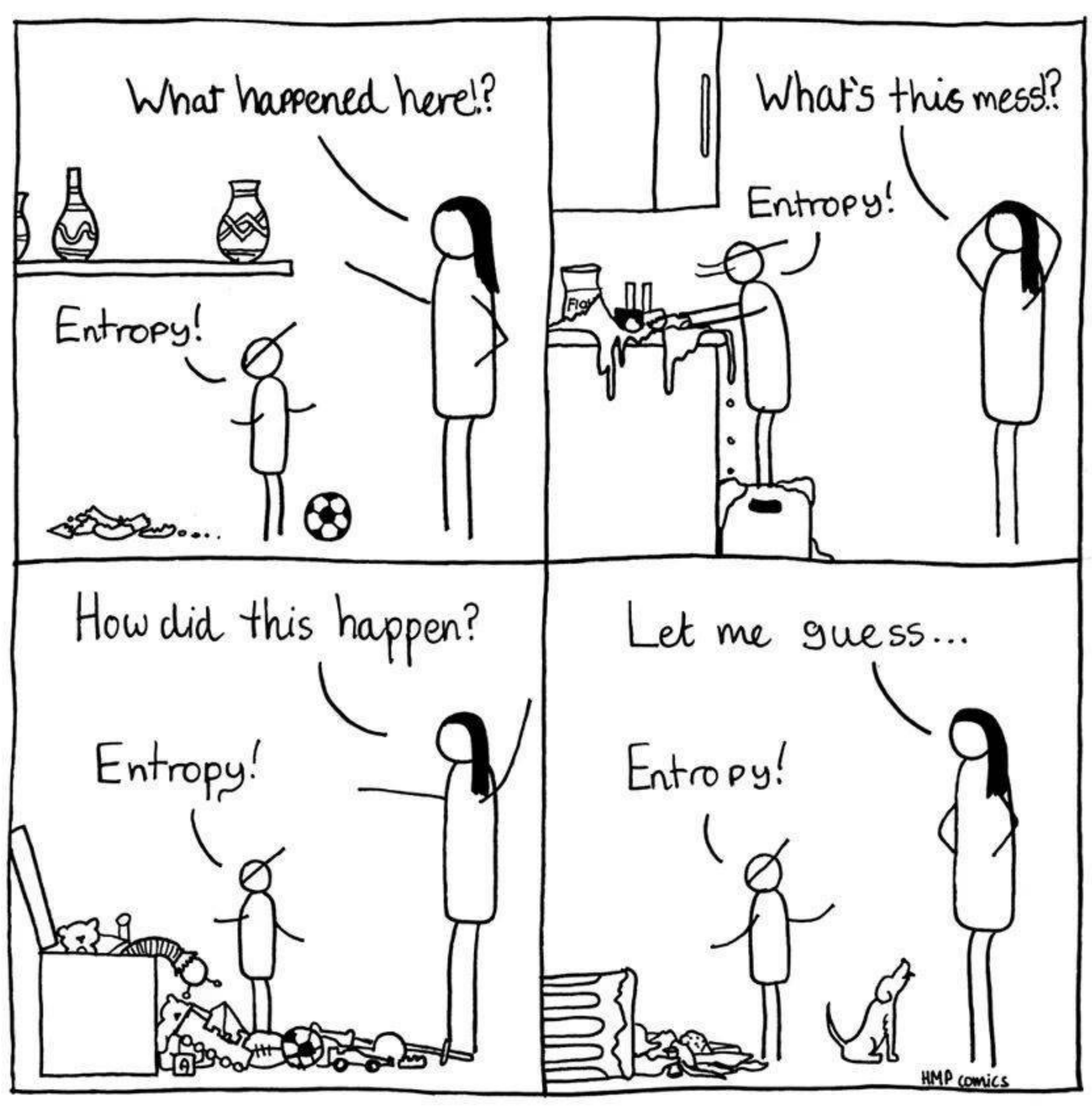
The unit label on ΔS^o could be

1. J
2. $\frac{J}{mol}$
3. $\frac{J}{mol \cdot K}$
4. $\frac{J}{g}$
5. $\frac{J}{^{\circ}C}$
6. $\frac{J}{g^{\circ}C}$
7. kJ
8. $\frac{kJ}{mol}$
9. $\frac{kJ}{mol \cdot {}^{o}F}$

The unit label on ΔS^o could be

1. J
2. $\frac{J}{mol}$
3. $\frac{J}{mol \cdot K}$
4. $\frac{J}{g}$
5. $\frac{J}{{}^\circ C}$
6. $\frac{J}{g\ {}^\circ C}$
7. kJ
8. $\frac{kJ}{mol}$
9. $\frac{kJ}{mol \cdot F}$

This is why we don't teach children about entropy until much later.



Two Forces Drive Reactions

- Low energy is favored
  - ✓ ΔH decrease (−) is thermodynamically favorable
  - ✓ You are aware that exothermic reactions are favorable reactions
    - combustion reactions

Energy *AND* Entropy drive reactions

- High entropy is favored
  - ✓ΔS increase (+) is favored
- For spontaneous processes with unfavorable energy change, the entropy change must be favorable.
  - ✓$H_2O_{(s)} \rightarrow H_2O_{(L)}$

Spontaneity
Thermodynamic Favorability

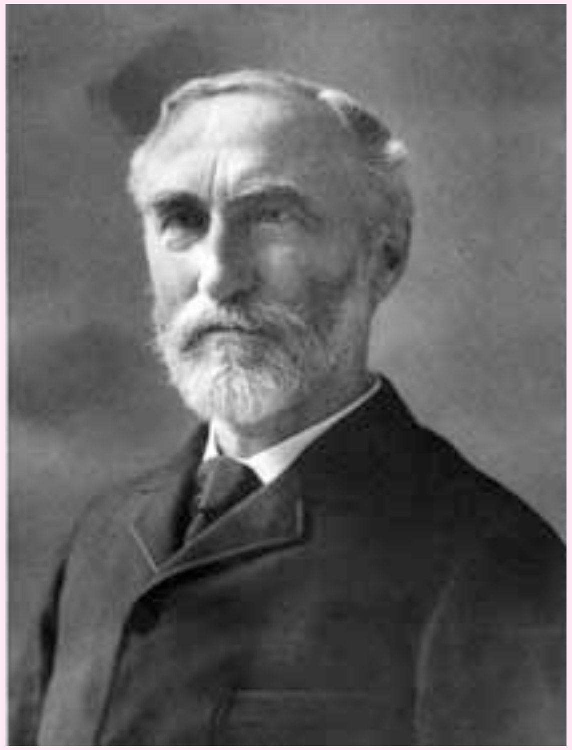
What drives reactions?

How can we mathematically combine energy and entropy?

What information do we need to know in order to predict the spontaneity of a process?

So how can we predict spontaneity?

- Josiah Willard Gibbs (USA) in 1873 combined enthalpy and entropy, the two driving forces into one mathematical relationship
- Gibbs Free Energy (G).
  - ✓ $\Delta G = \Delta H - T\Delta S$
  - ✓ ΔG is a measure of the spontaneity of a process and the "useful" energy available from a reaction.
  - ✓ ΔH is enthalpy
  - ✓ ΔS is entropy
  - ✓ T is temperature in Kelvin



1839-1903

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

- If $\Delta G < 0$, a reaction will proceed in the forward direction and is considered thermodynamically favorable (aka spontaneous).
- If $\Delta G > 0$, a reaction will not proceed in forward direction and is considered thermodynamically unfavorable (aka not spontaneous).

Using ΔG^o

- Standard conditions
  - ✓ 1 atm
  - ✓ 1 M concentration
- The ΔG^o values in the table are reported for temperatures at 25°C
- ΔG_f^o values have been established for many substances making the ΔG^o calculation at 1 M or 1 atm and *for 25°C*.
- $\Delta G^o_{Rx} = \sum n\Delta G_f^o{}_{prod} - \sum n\Delta G_f^o{}_{react}$

Use the thermodynamic tables to calculate ΔG^{o}_{298} (at 25ºC)

(º refers to standard conditions: 1atm and 1M)

(Because temperature is not a standard condition like pressure and molarity, the subscript number gives the particular temperature. If no number is given, assume 298 K.)

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

Use the thermodynamic tables to calculate ΔG^o_{298} (at 25ºC)

(º refers to standard conditions: 1atm and 1M)
(the subcript number give the temperature)

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

$\Delta G^o_f\ SO_{2(g)} = -300.4\,kJ$

$\Delta G^o_f\ SO_{3(g)} = -370.4\,kJ$

$\Delta G^o_f\ O_{2(g)} = 0\ kJ$

Use the thermodynamic tables to calculate ΔG^{o}_{298} at 25ºC

(º refers to standard conditions: 1atm and 1M)

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

- $\Delta G_{rx}{}^{o} = \sum n\Delta G_{f}{}^{o}{}_{prod} - \sum n\Delta G_{f}{}^{o}{}_{react}$
- $[2(-300.4\text{kJ/mol}) + 0\text{kJ/mol}] - [2(-370.4\text{kJ/mol})]$
- $\Delta G^{o}_{rx} = +140\ \text{kJ/mol}_{rx}$ (per reaction as written)
- If you put 1 atm (standard) of each substance in a container, the reaction would not proceed in the forward direction, but it would proceed in the reverse direction.
- A positive ΔGº does not mean that nothing happens, it simply means that the reaction favors reactants NOT products.

Use the thermodynamic tables to calculate ΔHº and ΔSº at 25ºC

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

$\Delta H^o_f\ SO_{2(g)} = -296.9$ kJ	$S^o\ SO_{2(g)} = 248.5$ J
$\Delta H^o_f\ SO_{3(g)} = -395.2$ kJ	$S^o\ SO_{3(g)} = 256.2$ J
$\Delta H^o_f\ O_{2(g)} = 0$ kJ	$S^o\ O_{2(g)} = 205$ J

Use the thermodynamic tables to calculate ΔHº and ΔSº at 25ºC

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

- $\Delta H = [2(-296.9) + 0] - 2(-395.2)$
  - $\Delta H = +196.6\ kJ/mol_{rx}$
    - ✓ (which is to say per 2 mol of SO_3, per 2 mol of SO_2, per 1 mol of O_2)

- $\Delta S = [2(+248.5) + 205] - 2(256.2)$
  - $\Delta S = +189.6\ J/mol_{rx}\ K$
    - ✓ (which is to say per 2 mol of SO_3, per 2 mol of SO_2, per 1 mol of O_2)

Using the ΔHº and ΔSº just calculated, use them to calculate ΔGº with Gibbs Free Energy Formula at 25ºC.

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

- $\Delta G^o = \Delta H^o - T\Delta S^o$
- $\Delta H = [2(-296.9) + 0] - 2(-395.2)$
  - $\Delta H = +196.6$ kJ/mol$_{rx}$
- $\Delta S = [2(+248.5) + 205] - 2(256.2)$
  - $\Delta S = +189.6$ J/mol$_{rx}$ K

Using the ΔH^o and ΔS^o just calculated, use them to calculate ΔG^o with Gibbs Free Energy Formula at 25ºC.

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

- $\Delta G^o = \Delta H^o - T\Delta S^o$
  - Watch out for the units!!
  - $\Delta G = +196.6\text{kJ} - [298\text{K}(0.1896\text{kJ/K})] = +140 \text{ kJ/mol}$

- $\Delta S = +189.6 \text{ J/mol}_{rx}\text{ K}$
- $\Delta H = +196.6 \text{ kJ/mol}_{rx}$

- How does it compare to the previously calculated with ΔG_f^o values?
  - the same since it was all for 25º.

So What Formulas Should I be able to use?

Get out your formula sheet.

So what formulas do we know how to use in this unit?

q = heat
m = mass
c = specific heat capacity
T = temperature
S° = standard entropy
H° = standard enthalpy
G° = standard free energy
n = number of moles

- $q = \mathrm{m}\times\mathrm{c}\times\Delta\mathrm{T}$ $\boxed{q = mc\Delta T}$
- $q = \mathrm{C}\times\Delta\mathrm{T}$ (not on the formula sheet)
- $q = \Delta\mathrm{H}\times\text{amount}$ (not on the formula sheet)
- $\Delta H^o{}_{Rx} = \sum \mathrm{n}\Delta H_f{}^o{}_{prod} - \sum \mathrm{n}\Delta H_f{}^o{}_{react}$

  $\boxed{\Delta H^\circ = \sum \Delta H_f^\circ \text{ products} - \sum \Delta H_f^\circ \text{ reactants}}$
- *Hess' Law* (not on the formula sheet)
- $\Delta S^o{}_{Rx} = \sum \mathrm{n}\Delta S^o{}_{prod} - \sum \mathrm{n}\Delta S^o{}_{react}$ $\boxed{\Delta S^\circ = \sum S^\circ \text{ products} - \sum S^\circ \text{ reactants}}$
- $\Delta \mathrm{G^o} = \Delta \mathrm{H^o} - \mathrm{T}\Delta \mathrm{S^o}$ $\boxed{\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ}$
- $\Delta G^o{}_{Rx} = \sum \mathrm{n}\Delta G_f{}^o{}_{prod} - \sum \mathrm{n}\Delta G_f{}^o{}_{react}$

  $\boxed{\Delta G^\circ = \sum \Delta G_f^\circ \text{ products} - \sum \Delta G_f^\circ \text{ reactants}}$

What about calculating ΔG at different temperatures?

Calculating ΔG^o_{Temp} at other than 25º

- Conditions are often NOT at 25ºC.
- ΔG^o is *very* temperature dependent
  - ✓ notice the T in the formula $\Delta G^o = \Delta H^o - T\Delta S^o$
- When not at 25º
  - ✓ You can *not* use $\Delta G_{Rx}{}^o = \sum n\Delta G_f{}^o{}_{prod} - \sum n\Delta G_f{}^o{}_{react}$
    - because ΔG_f^o values are listed *only* for 25ºC
  - ✓ You *must* use $\Delta G^o{}_{temp} = \Delta H^o - T\Delta S^o$
- How can we get away with this?
  - ✓ ΔH^o and ΔS^o are NOT so very temp dependent, thus a decent estimation of $\Delta G^o{}_{temp}$ can be determined at different temperatures using Gibbs Equation.

Using the ΔHº and ΔSº previously calculated and the Gibbs Free Energy Formula, to calculate free energy at 1127ºC, which is 1400K.

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

- $\Delta G^{o}_{1400.} = \Delta H^{o} - T\Delta S^{o}$
- $\Delta H^{o} = +196.6\ \text{kJ/mol}_{rx}$
- $\Delta S^{o} = +189.6\ \text{J/mol}_{rx}\text{K}$

Using the ΔHº and ΔSº previously calculated and the Gibbs Free Energy Formula, calculate free energy at 1127ºC

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

$\Delta G^{o}_{T,1400}$ at 1400 K?

$$\Delta G^{o} = \Delta H^{o} - T\Delta S^{o}$$

- $\Delta S = +189.6\ J/mol_{rx}\ K$
- $\Delta H = +196.6\ kJ/mol_{rx}$

- Watch out for the units!!
- $\Delta G = +196.6 kJ/rx - [1400\ K\ (0.1896 kJ/rxK)] = -68.84 kJ/rx$
- This is spontaneous! Say whaaaat!!
- at 298 K the Rx was NOT spontaneous, $+140\ kJ/mol_{rx}$

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

$\Delta H^o = +196.6$ kJ and $\Delta S^o = 0.1896$ kJ

- This reaction is *not* spontaneous at room temperature
  - ($\Delta G^o_{298} = +140$kJ),
- This reaction *is* spontaneous at 1127°C
  - ($\Delta G^o_{1400} = -68.84$kJ),
- at what temperature (in °C) does the spontaneity change from spontaneous to not spontaneous?

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

- $\Delta S = +189.6\ \text{J/mol}_{rx}\ \text{K}$
- $\Delta H = +196.6\ \text{kJ/mol}_{rx}$

If this reaction is not spontaneous at room temperature ($\Delta G^o_{298} = +140\text{kJ}$), and it is spontaneous at 1127ºC ($\Delta G^o_{1400} = -68.84\text{kJ}$), at what temperature (in ºC) does the spontaneity change from spontaneous to not spontaneous?

- $\Delta G^o = \Delta H^o - T\Delta S^o$
- The sign of ΔGº changes when ΔGº = 0, solve for T
- $0 = +196.6\text{kJ} - T(0.1896\text{kJ/K})$
- T = 1037 K, which is 764ºC

→

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

- ΔH^o = +196.6 kJ/for the reaction
- ΔS^o = +189.6 J/K for the reaction

If this reaction is *not* spontaneous at room temperature, 25ºC (ΔG^o_{298} = +140kJ), and it *is* spontaneous at 1037ºC (ΔG^o_{1400} = −68.84kJ)

What happens at 764ºC?

1. The reaction “stops.”
2. The reaction is at equilibrium.
3. It depends on if you start above or below 764ºC.
4. Some other situation.

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

If this reaction is *not* spontaneous at room temperature, 25ºC (ΔG^o_{298} = +140kJ), and it *is* spontaneous at 1037ºC (ΔG^o_{1400} = −68.84kJ)

What happens at 764ºC?

1. The reaction “stops.”
   - *Really, we know this means the forward and reverse reactions are happening at the same speed.*
2. The reaction is at equilibrium, since $\Delta G^o_{1037} = 0$
3. It depends on if you start above or below 764ºC
4. Some other situation.

What is $\Delta G = 0$?

- If $\Delta G^o < 0$ the reaction is spontaneous
- if $\Delta G^o > 0$ the reaction is *not* spontaneous
- What is $\Delta G = 0$?
  - ✓ Equilibrium
  - ✓ There is no “net” movement of the reaction in the forward direction or the reverse direction – No changes of concentrations or amounts of reactants or products.
  - ✓ You know this is the moment at which the rate of the forward reaction equals the rate of the reverse reaction.

The reaction below is NOT spontaneous at 298 K. Without making any calculations, is there a temperature at which this reaction can become spontaneous?

$2NOCl_{(g)} \rightarrow 2NO_{(g)} + Cl_{2(g)}$

For the reaction: $\Delta H^o = +74$ kJ, $\Delta S^o = +117$ J

1. Yes
2. No
3. Not enough information to determine.

The reaction below is NOT spontaneous at 298 K. Without making any calculations, is there a temperature at which this reaction can become spontaneous?

$2NOCl_{(g)} \rightarrow 2NO_{(g)} + Cl_{2(g)}$

For the reaction: $\Delta H^{o} = +74$ kJ, $\Delta S^{o} = +117$ J

1. Yes
2. Whenever ΔS is favorable (+), the possibility exists for a large enough T to make $|T\Delta S|$ large enough to counteract the unfavorable ΔH
3. No
4. Not enough information to determine.

The reaction below is NOT spontaneous at 298 K. Without making any calculations, is there a temperature at which this reaction can become spontaneous?

$R \rightarrow P$

For the reaction: $\Delta H^\circ < 0$ and $\Delta S^\circ < 0$

1. Yes
2. No
3. Not enough information to determine.

The reaction below is NOT spontaneous at 298 K. Without making any calculations, is there a temperature at which this reaction can become spontaneous?

$X \rightarrow Y$

For the reaction: $\Delta H^o < 0$ and $\Delta S^o < 0$

1. Yes
   - Whenever ΔS is unfavorable (−), the possibility exists for a small enough T to make $|T\Delta S|$ small enough to be overtaken by the favorable ΔH
   - Remember, when the sign of ΔS and ΔH are the same, spontaneity can be changed with temperature changes.
2. No
3. Not enough information to determine.

The reaction below is NOT spontaneous at 298 K. Without making any calculations, is there a temperature at which this reaction can become spontaneous?

$2\,A \rightarrow 3\,B$

For the reaction: $\Delta H^o > 0$ and $\Delta S^o < 0$

1. Yes
2. No
3. Not enough information to determine.

The reaction below is NOT spontaneous at 298 K. Without making any calculations, is there a temperature at which this reaction can become spontaneous?

$2\,A \rightarrow 3\,B$

For the reaction: $\Delta H^\circ > 0$ and $\Delta S^\circ < 0$

1. Yes
2. No
   - Whenever $\Delta S(-)$ and $\Delta H(+)$ are both unfavorable, ΔG can never be spontaneous $(-)$.
3. Not enough information to determine.

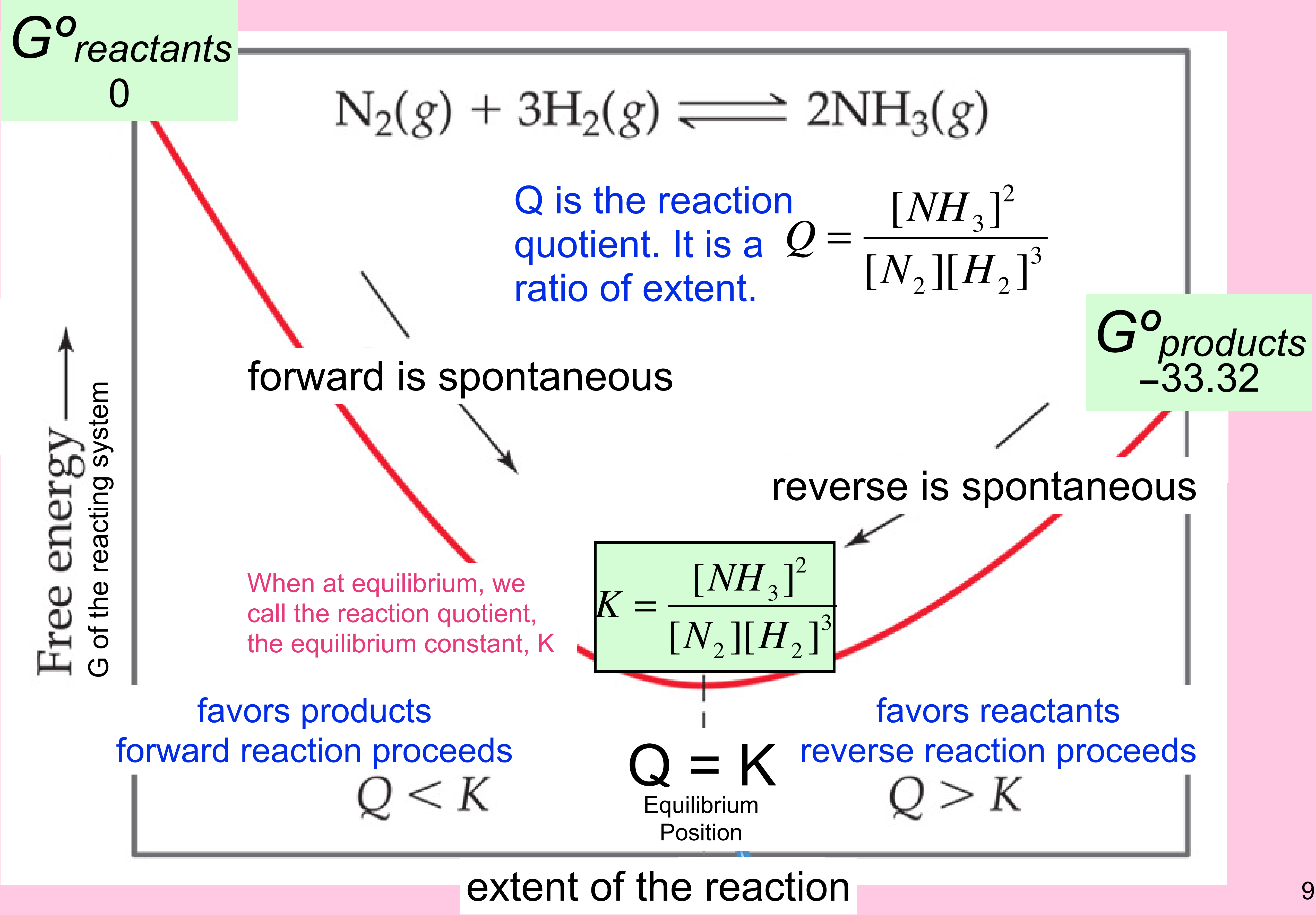
Consider the effect of temperature on spontaneity. Remember Kelvin temps are always positive

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

ΔH	ΔS	ΔG
– favorable	+ favorable	is *always* (spontaneous) thermodynamically favorable
+ unfavorable	– unfavorable	is *never* spontaneous
– favorable	– unfavorable	Spontaneous only if $\lvert\Delta H\rvert > \lvert T\Delta S\rvert$ lower T favors spontaneity
+ unfavorable	+ favorable	Spontaneous only if $\lvert\Delta H\rvert < \lvert T\Delta S\rvert$ higher T favors spontaneity

How is ΔG related to K?

Reversible Reactions



$G^o_{reactants}$
0

Q is the reaction quotient. It is a ratio of extent.

$$Q = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

$G^o_{products}$
–33.32

forward is spontaneous

reverse is spontaneous

When at equilibrium, we call the reaction quotient, the equilibrium constant, K

$$K = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

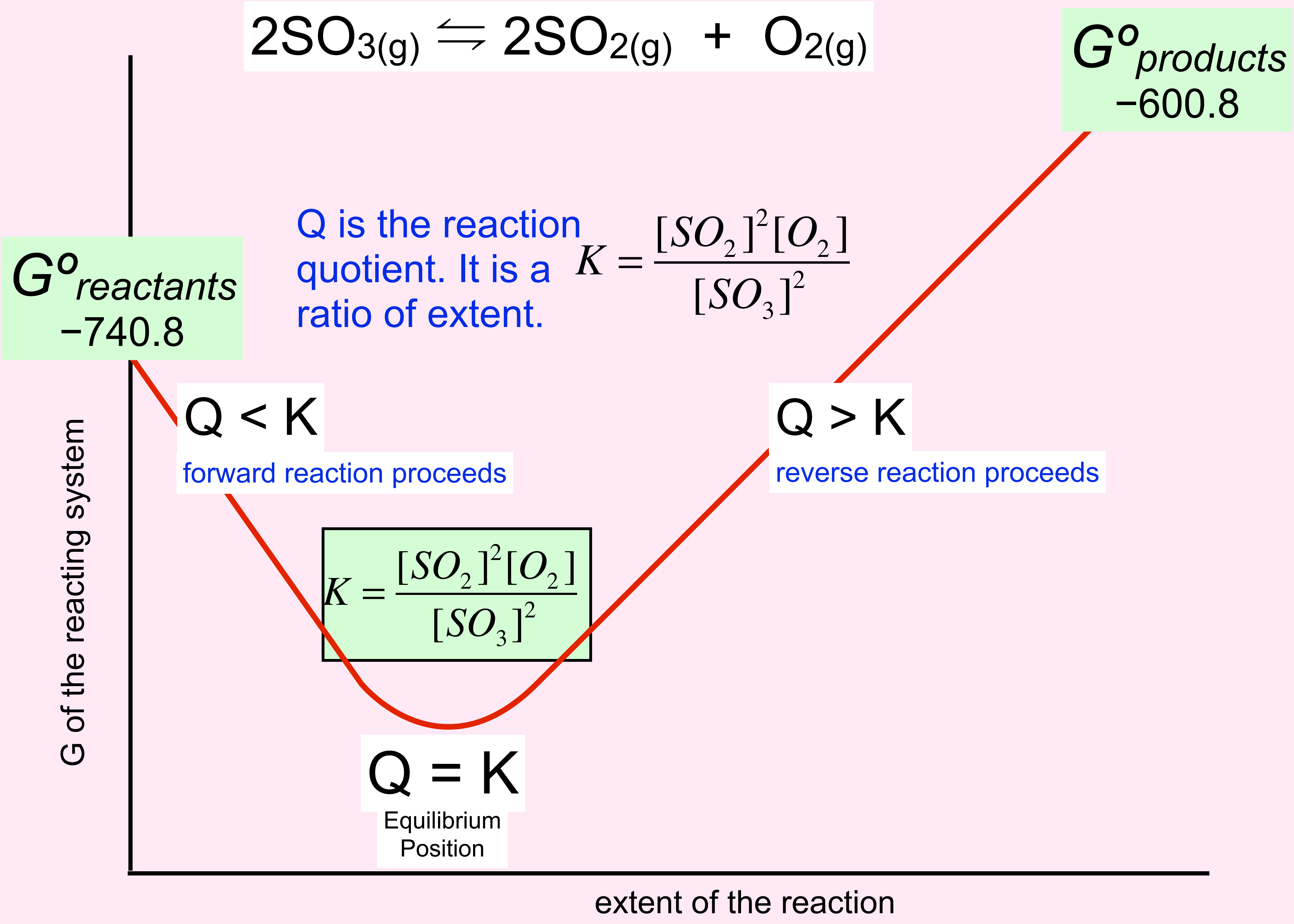
favors products
forward reaction proceeds

Q = K
Equilibrium
Position

favors reactants
reverse reaction proceeds

extent of the reaction

Reversible Reactions



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

$G^o_{products}$
−600.8

$G^o_{reactants}$
−740.8

Q is the reaction quotient. It is a ratio of extent.

$$K = \frac{[SO_2]^2[O_2]}{[SO_3]^2}$$

Q < K

forward reaction proceeds

Q > K

reverse reaction proceeds

$$K = \frac{[SO_2]^2[O_2]}{[SO_3]^2}$$

Q = K

Equilibrium
Position

How does concentration affect ΔG ?

So we know how to calculate ΔG^o at temperatures other than 298 K, (using $\Delta G^o_{temp} = \Delta H^o - \mathrm{T}\Delta S^o$)

what if we want to know $\Delta \mathrm{G}$ at non-standard conditions: pressures other than 1 atm or concentrations other than 1 M?

- *We need a new equation….*

So we know how to calculate ΔG^o at temperatures other than 298 K, using $\Delta G^o_{temp} = \Delta H^o - T\Delta S^o$

what if we want to know ΔG at non-standard conditions: pressures other than 1 atm or concentrations other than 1 M?

The relationship between ΔG and ΔG^o can be calculated with the following mathematical relationship:

$$\Delta G_{temp} = \Delta G^o_{temp} + RT \ln Q$$

Many scientists spent their entire adult careers sorting out these mathematical relationships....it is not possible for us, at this time to "understand" where these relationships come from, or how they were figured out. We simply need to appreciate them and be able to use them.

ΔG_{temp} at nonstandard pressure & concentration

- $\Delta G_{temp} = \Delta G^{o}_{temp} + RT\ \ln Q$
  - ✓ R = 8.314 J/mole K (the gas constant in energy units)
  - ✓ T is always in Kelvin
  - ✓ Q is the reaction quotient
    - ‣ Right-side over left side raised to their equation coefficients.
- If temp = 298
  - ✓ calculate ΔG° using $\Delta G^{o}_{Rx} = \sum n\Delta G_{f}^{o}{}_{prod} - \sum n\Delta G_{f}^{o}{}_{react}$
  - ✓ then use formula above to calculate ΔG (nonstandard pressure or concentration
- If temp is something other than 298
  - ✓ calculate ΔG^{o}_{temp} using $\Delta G^{o}_{temp} = \Delta H^{o} - T\Delta S^{o}$
  - ✓ then use formula above to calculate ΔG (nonstandard pressure or concentration

What is “ln” ? Natural Log

- $\Delta G_{temp} = \Delta G^{o}_{temp} + RT \ln Q$
- so what is lnQ?
- Find the the ln (not log, base 10) key on your calculator.
- For now we will simply accept that taking the natural log of Q is a mathematical tool to analyze the progress of the reaction i.e. the difference between the products and reactants.
- This is what we need to do in order to solve the mathematical equation above.

natural log Facts

ln(or log)(# > 1)	+
ln (or log)(1)	0
ln (or log)(# < 1 & bigger than zero)	−

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

- When Q=1, ln=0, $\Delta G = \Delta G^{o}$
- If products increase, Q >1, ln+, ΔG is more positive and less thermodynamically favorable
- If reactants increase, Q <1, ln−, ΔG is more negative and less thermodynamically favorable

How is ΔG related to K?

The Relationship between ΔG and K

- $\Delta G_{temp} = \Delta G^{o}_{temp} + RT\ lnQ$

- When at equilibrium,
  - ✓ $\Delta G_{temp} = 0$, and $Q = K_{eq}$

- the equation at the top becomes
  - ✓ $0 = \Delta G^{o}_{temp} + RT\ lnK$

- and let solve for ΔG^{o}_{temp},
  - ✓ $\Delta G^{o}_{temp} = -RT\ lnK$

Calculate $\Delta G^o_{T,\,300K}$ in kJ/mole for a reaction at 300K in which
$K_{eq} = 2.2 \times 10^{-4}$

Round to the nearest whole number - You may use your calculator.

Submit your answer rounded to the nearest whole number.

Calculate $\Delta G^{o}_{T,\ 300K}$ in kJ/mole for a reaction at 300K in which $K_{eq} = 2.2\text{x}10^{-4}$

Round to the nearest whole number − You may use your calculator.

- $\Delta G^{o} = -RT \ln K$
- $\Delta G^{o} = -(0.008314\ \text{kJ/K})(300\text{K})(\ln 2.2\text{x}10^{-4})$
- +21 kJ/mol   or 21,000J/mol

$2SO_{3(g)} \rightarrow 2SO_{2(g)} + O_{2(g)}$ (on slide 76)

We used the ΔH^o and ΔS^o and the Gibbs Free Energy Formula ($\Delta G = \Delta H - T\Delta S$), to calculate free energy at 1127ºC (1400. K)

$\Delta G^o_{T=1400.} = -69.0 \text{ kJ}$

Calculate K for this reaction at this temp.

The algebraic inverse of $\ln(K) = x$ is $K = e^x$

Find this on your calculator. Notice that it is the second function of ln.

(Just as the second function x^2 of is $\sqrt{x}$)

Having use the ΔHº and ΔSº previously calculated and the Gibbs Free Energy Formula, $\Delta G^{o}_{T=1400} = -69\text{kJ}$. Use this info to calculate free energy at 1127ºC

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

$$\frac{-69}{-(0.008314)(1400)} = \ln K$$

$\Delta G^{o}_{T,1400.} = -69\text{kJ}$

$\Delta G^{o}_{T,1400.} = -RT\ \ln K$

$-69\text{ kJ} = -(0.00831\text{ kJ})(1400.\text{K})\ln K$

$$e^{\frac{-69}{-(0.008314)(1400)}} \quad thus \quad e^{5.928} = K$$

K = 375, large, thermodynamically favored as you would expect by the negative ΔG

Need more practice with your calculator? Calculate K for a reaction at 25ºC in which

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

1. $\Delta G^\circ = -4$ kJ/mol$_{rxn}$
2. $\Delta G^\circ = +12$ kJ/mol$_{rxn}$
3. $\Delta G^\circ = 0$ kJ/mol$_{rxn}$

$$\frac{\Delta G^\circ}{-(0.00831)(298)} = \ln K$$

$$e^{\frac{\Delta G^\circ}{-(0.00831)(298)}} = K$$

Need more practicewith your calculator? Calculate K for a reaction in which

1. $\Delta G^\circ = -4$
   - K = 5
2. $\Delta G^\circ = +12$
   - K = 0.0079
3. $\Delta G^\circ = 0$
   - K = 1

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

$$\frac{\Delta G^\circ}{-(0.00831)(298)} = \ln K$$

$$e^{\frac{\Delta G^\circ}{-(0.00831)(298)}} = K$$

Calculate the free energy at 25ºC

$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_{2(g)} + 6H_2O_{(L)}$

$\Delta G^o_{T,298} = -2879\ \text{kJ}$

Calculate K for this reaction at 25ºC

Calculate the free energy at 25ºC

$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_{2(g)} + 6H_2O_{(L)}$

$\Delta G^o_{T,298} = -2879$ kJ

Calculate K for this reaction at 25ºC

$K = 4.58 \times 10^{504}$ (this is ridiculously huge!!)

On most calculators, this will give you an error readout, because most calculators will only produce scientific notation up to 10^{99}

Relationship of ΔG^o and K

- $\Delta G^o_{temp} = -RT \ln K_{eq}$
- If $\Delta G^o < 0$ then $K > 1$
  - ✓ natural log of any number larger than 1 is a positive #
- If $\Delta G^o = 0$ then $K = 1$ ($\ln K = 0$)
  - ✓ Since at standard conditions 1 M and 1 atm
  - ✓ and natural log of 1 = 0
- If $\Delta G^o > 0$ then $K < 1$
  - ✓ natural log of any number smaller than 1 is a negative #

Free Energy and Electrical Energy

The relationship between ΔG and E_{cell}

Free Energy, ΔG and Electrochem, E

- Remember, a reaction is thermodynamically favored when
  - ✓ $E_{cell} > 0$
  - ✓ $\Delta G_{rxn} < 0$
  - ✓ A more positive E_{cell} gives rise to a more negative ΔG

- E_{cell} is measured in V, volts
  - ✓ 1 volt = 1 Joule per coulomb
  - ✓ A coulomb is the charge on 6.242×10^{18} electrons

$\Delta G^o = -n\mathscr{F}E^o$

- Let's consider why the need for the negative sign
  - ✓ ΔG is negative = spontaneous
  - ✓ E is positive = spontaneous
- ΔG = free energy
  - ✓ usually kJ mol^{-1}
- n = mole of electrons transferred/mole of Rxn
- F = the Faraday, 96,485 coulombs/mol e^-
- E = potential (voltage), joules/coulomb

Consider a aluminum / cadmium voltaic cell made with each metal and their respective nitrate solutions at room temperature, 25ºC.

1. Write the balanced net ionic equation and calculate the voltage, Eº
2. Calculate free energy, ∆Gº

reduction half-reaction	$E^o_{reduction}$ **(V)**
$Cd^{2+} + 2e^- \rightarrow Cd$	-0.40
$Al^{3+} + 3e^- \rightarrow Al$	-1.66

Consider a aluminum / cadmium voltaic cell made with each metal and their respective nitrate solutions at room temperature, 25ºC.

reduction half-reaction	$E^o_{reduction}$ (V)
$Cd^{2+} + 2e^- \rightarrow Cd$	-0.40
$Al^{3+} + 3e^- \rightarrow Al$	-1.66

- $2Al + 3Cd^{2+} \rightarrow 2Al^{3+} + 3Cd$
- $E^o_{cell} = +1.26$ V
- Remember, one of the half reactions must be reversed to oxidation, to combine with a reduction.
- For voltaic cell the voltage must end up positive.
- The cadmium reduction reaction must be tripled, the aluminum oxidation must be doubled so that the electrons transferred are the same = 6, but do NOT double the voltage

1. Calculate free energy, ΔG^o

Consider a aluminum / cadmium voltaic cell made with each metal and their respective nitrate solutions at room temperature, 25ºC.

reduction half-reaction	$E^o_{reduction}$ (V)
$Cd^{2+} + 2e^- \rightarrow Cd$	-0.40
$Al^{3+} + 3e^- \rightarrow Al$	-1.66

- $2Al + 3Cd^{2+} \rightarrow 2Al^{3+} + 3Cd$
- $E^o_{cell} = +1.26$ V
- n = six electrons transferred

$$\Delta G^o = -nFE^o$$

- Calculate free energy, ΔG^o
- $\Delta G^o = -729$ kJ/mol

$$\Delta G^o = -(6 mol\ e^-)\left(96{,}485 \frac{coul}{mole-}\right)\left(1.26 \frac{Joule}{coul}\right)$$

How does concentration affect voltage of a cell ?

The Nernst Equation

Effect of Concentration on Cell Potential, E

Don't write….just watch.

- Remember $\Delta G = \Delta G^o + RT \ln Q$
- and we now know $\Delta G^o = -nFE^o$
- substitute $-nFE = -nFE^o + RT \ln Q$
- divide through by −nF $E = E^o - \dfrac{RT}{nF} \ln Q$

$$E = E^o - \frac{8.314\frac{J}{molK} \times 298K}{n \times 96{,}485\frac{coul}{mol\ e^-}} \ln Q$$

remember, a J/coul = Volt

$$E = E^o - \frac{0.0257}{n} \ln Q$$

many texts convert natural log to base 10 log: multiply by 2.303

$$E = E^o - \frac{0.0592}{n} \log Q$$

For the following reaction from a Galvanic cell

$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$ $E^{o} = 1.10\ V$

Would the voltage of the Galvanic cell that was set up with $[Cu^{2+}] = 2M$ and $[Zn^{2+}] = 0.1M$

1. increase
2. decrease
3. stay the same

For the following reaction from a Galvanic cell

$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$ $E^o = 1.10$ V

Would the voltage of the Galvanic cell that was set up with $[Cu^{2+}] = 2M$ and $[Zn^{2+}] = 0.1M$

1. increase
2. decrease
3. stay the same

$$Q = \frac{\left[Zn^{2+}\right]}{\left[Cu^{2+}\right]} \quad = \frac{[0.1]}{[2]} \quad Q < 1$$

$$E = E^o - \#\# \log Q$$

When Q <1, logQ is negative, thus voltage increases

For the following reaction from a Galvanic cell

$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu \quad E^{o} = 1.10\ V$

Would the voltage of the Galvanic cell that was set up with $[Cu^{2+}] = 2M$ and $[Zn^{2+}] = 3M$

1. increase
2. decrease
3. stay the same

For the following reaction from a Galvanic cell

$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$ $E^o = 1.10\ V$

Would the voltage of the Galvanic cell that was set up with $[Cu^{2+}] = 2M$ and $[Zn^{2+}]= 3M$

1. increase
2. decrease
3. stay the same

$$Q = \frac{\left[Zn^{2+}\right]}{\left[Cu^{2+}\right]} \quad = \frac{[3]}{[2]} \quad Q > 1$$

$$E = E^o - \#\# \log Q$$

When Q >1, logQ is positive, thus voltage decreases

For the following reaction from a Galvanic cell

$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$ $E^o = 1.10$ V

Would the voltage of the Galvanic cell that was set up with $[Zn^{2+}] = 0.5M$ and $[Cu^{2+}] = 0.5M$

1. increase
2. decrease
3. stay the same

For the following reaction from a Galvanic cell

$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$ $E^o = 1.10$ V

Would the voltage of the Galvanic cell that was set up with $[Zn^{2+}] = 0.5M$ and $[Cu^{2+}] = 0.5M$

1. increase
2. decrease
3. stay the same

$$Q = \frac{\left[Zn^{2+}\right]}{\left[Cu^{2+}\right]} \quad = \frac{[0.5]}{[0.5]} \quad Q = 1$$

$$E = E^o - \#\#\log Q$$

When Q =1, logQ is zero, thus voltage stays the same

Consider a lead / silver voltaic cell made with each metal and their respective nitrate solutions at room temperature, 25°C.

1. Write the balanced net ionic equation and calculate the voltage, E°
2. Calculate free energy, ΔG°
3. Calculate the equilibrium constant, K

reduction half-reaction	$E^{o}_{reduction}$ **(V)**
$Ag^{+} + 1e^{-} \rightarrow Ag$	0.80
$Pb^{2+} + 2e^{-} \rightarrow Pb$	-0.13

Consider a lead / silver voltaic cell made with each metal and their respective nitrate solutions.

1. Write the balanced net ionic equation and calculate the voltage, E°

reduction half-reaction	**$E^o_{reduction}$ (V)**
$Ag^+ + 1e^- \rightarrow Ag$	0.80
$Pb^{2+} + 2e^- \rightarrow Pb$	-0.13

- $Pb + 2Ag^+ \rightarrow Pb^{2+} + 2Ag$
- $E^o_{cell} = 0.93$ V
- Remember, one of the half reactions must be reversed to oxidation, to combine with a reduction.
- For voltaic cell the voltage must end up positive.
- The silver reduction reaction must be doubled, so the 2 electrons lost by the lead can both be collected by the two Ag, but do NOT double the voltage

Consider a lead / silver voltaic cell made with each metal and their respective nitrate solutions.

1. Write the balanced net ionic equation and calculate the voltage, E°

- $Pb + 2Ag^+ \rightarrow Pb^{2+} + 2Ag$
- $E^o_{cell} = 0.93\ V$

half-reaction	**E° (V)**
$Ag^+ + 1e^- \rightarrow Ag$	0.80
$Pb^{2+} + 2e^- \rightarrow Pb$	-0.13

2. Calculate free energy, ΔG°

- $\Delta G^o = -179\ kJ/mol$

$$\Delta G^o = -nFE^o$$

$$\Delta G^o = -(2 mole-)\left(96{,}485 \frac{coul}{mole-}\right)\left(0.93 \frac{Joule}{coul}\right)$$

Consider a lead / silver voltaic cell made with each metal and their respective nitrate solutions.

1. Write the balanced net ionic equation and calculate the voltage, E°

- $Pb + 2Ag^+ \rightarrow Pb^{2+} + 2Ag$
- Ag $E^o_{red} = 0.80$ V Pb^{2+} $E^o_{ox} = 0.13$ V $E^o_{cell} = 0.93$ V
- $\Delta G^o = -179$ kJ/mol

3. Calculate the equilibrium constant, K

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

$$\ln K = \frac{-180 kJ\ mol}{\left(0.00831 kJ\ \mathrm{mol}\ K^{-1}\right)\left(298 K\right)}$$

$$\ln K = 72.5$$

4. solve for K = 2.97×10^{31}

Consider a lead / silver voltaic cell made with each metal and their respective nitrate solutions.

- $Pb + 2Ag^{+} \rightarrow Pb^{2+} + 2Ag$
- $E^{o}_{cell} = 0.93$ V
- If this cell were set up with 0.5 M of each nitrate solution (instead of 1 M), would the voltage

1. increase,
2. decrease,
3. or stay the same?

Consider a lead / silver voltaic cell made with each metal and their respective nitrate solutions.

- $Pb + 2Ag^+ \rightarrow Pb^{2+} + 2Ag$
- $E^o_{cell} = 0.93\ V$
- If this cell were set up with 0.5 M of each nitrate solution (instead of 1 M), would the voltage

1. increase,
2. decrease,
3. or stay the same?

$$Q = \frac{\left[Pb^{2+}\right]}{\left[Ag^+\right]^2} = \frac{[0.5]}{[0.5]^2} \qquad Q = \frac{0.5}{0.25} = 2$$

$$E = E^o - \#\#\log Q$$

When Q >1, logQ is positive, thus voltage decreases

How are E^o, ΔG^o, and K interconnected?

First, let’s tie E° to K

Don’t write….just watch.

- We know: $\Delta G^o = -nFE^o$
- and we know: $\Delta G^o = -RT\ \ln K_{eq}$
- Set these two equations equal to each other
  - ✓ $-RT\ \ln K = -nFE^o$ then solve for E°
- Watch out for units:
  - $R = 8.314\ J/mol_{Rxn}\ K$
  - T = temperature in Kelvin
  - n = number of electrons transferred, per $mole_{Rxn}$
  - F = the Faraday, 96,485 C/mol
  - K = the equilibrium constant, unitless

$$E^o = \frac{RT}{nF}\ln K$$

Let’s go to the next slide and plug in these values.

→

Electrochem and Equilibrium

Don’t write….just watch.

$$E^o = \frac{RT}{nF}\ln K$$

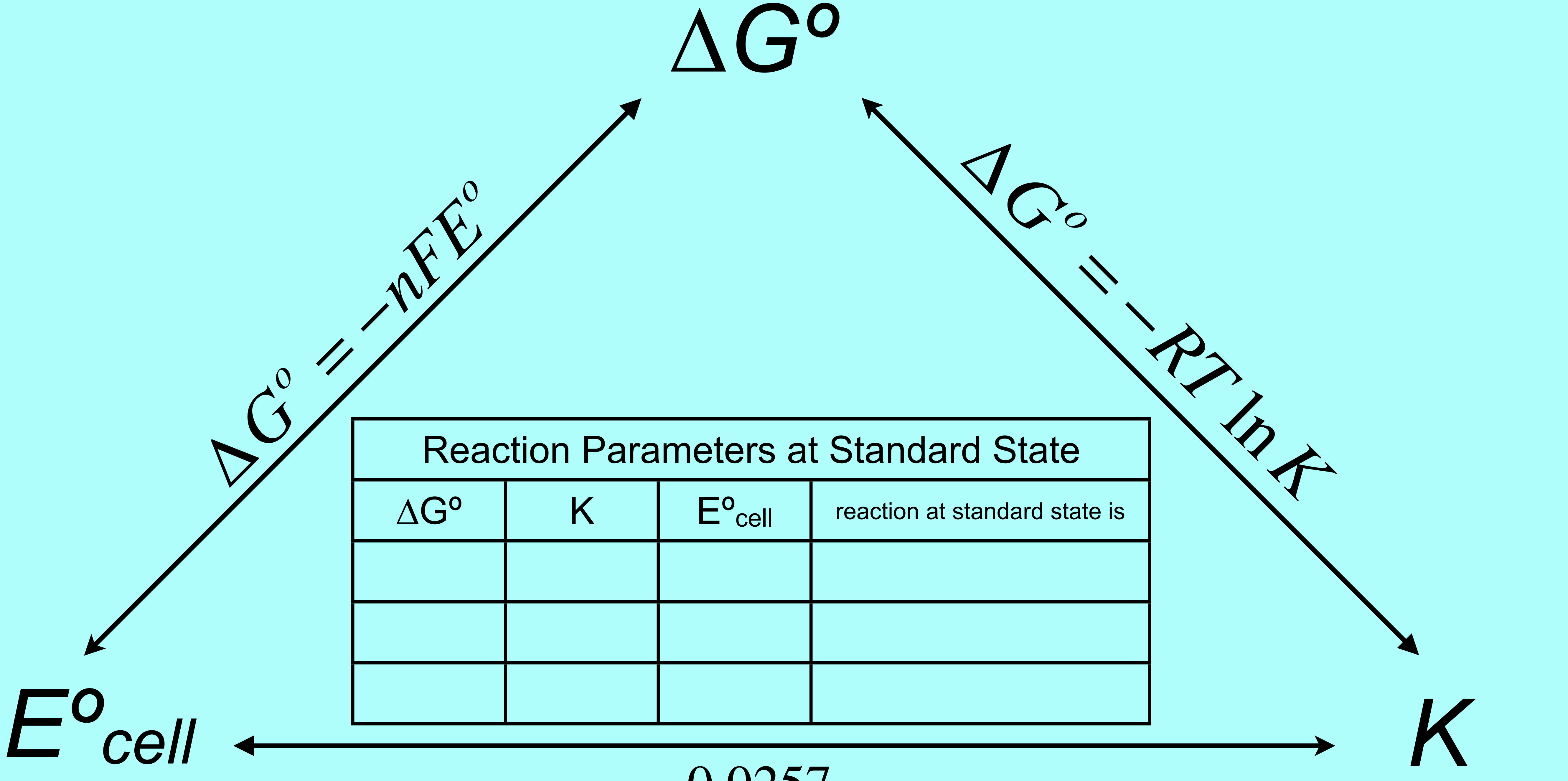
by definition 1 V = 1J/coul

$$E^o = 2.303\frac{\left(8.314\frac{J}{molRx \bullet K}\right)(298K)}{\left(n\frac{mol\ of\ e^-}{molRx}\right)\left(96{,}486\frac{coul}{mol\ of\ e^-}\right)}\ln K$$

$$E^o = \frac{0.0257V}{n}\ln K$$

This equation is NOT on the formula sheet.
You don’t really need it because you could always from *E°* to Δ*G°* to *K*
if necessary as we did on a previous slide.

Electrochem, Equilibrium, Free Energy



$$\Delta G^o = -nFE^o$$

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

Reaction Parameters at Standard State			
ΔG°	K	E^o_{cell}	reaction at standard state is

$$E^o = \frac{0.0257}{n} \ln K$$

This equation is NOT on the formula sheet.
You don’t really need it because you could always from *E*° to Δ*G*° to *K* if necessary.

Electrochem, Equilibrium, Free Energy

ΔG^o

$$\Delta G^o = -nFE^o$$

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

Reaction Parameters at Standard State			
ΔG^o	K	E^o_{cell}	reaction at standard state
−	> 1	+	Thermodynamically **Favorable**
0	1	0	at Equilibrium
+	< 1	−	Thermodynamically **Unfavorable**

E^o_{cell} $\longleftrightarrow$ K

$$E^o = \frac{0.0257}{n}\ln K$$

This equation is NOT on the formula sheet.
You don't really need it because you could always from E^o to ΔG^o to K if necessary.

Review
& More Practice

In which of the following conditions can you be sure about the spontaneity of a reaction?

	ΔH	ΔS
1	+	+
2	+	-
3	-	-
4	-	+

In which of the following conditions can you be sure about the spontaneity of a reaction?

- For # 2 we know that it will never be spontaneous since both ΔH and ΔS are unfavorable.
- For # 4 we know that it will always be spontaneous since both ΔH and ΔS are favorable.

	ΔH	ΔS
1	+	+
2	+	-
3	-	-
4	-	+

Select the set of thermodynamic parameters that best describes the system below at room conditions

$H_2O_{(s)} \leftrightharpoons H_2O_{(L)}$

	ΔG	ΔH	ΔS	ΔVolume
1	$\Delta G = 0$	$\Delta H > 0$	$\Delta S > 0$	$\Delta V > 0$
2	$\Delta G = 0$	$\Delta H > 0$	$\Delta S < 0$	$\Delta V = 0$
3	$\Delta G < 0$	$\Delta H > 0$	$\Delta S < 0$	$\Delta V < 0$
4	$\Delta G < 0$	$\Delta H > 0$	$\Delta S > 0$	$\Delta V < 0$
5	$\Delta G < 0$	$\Delta H < 0$	$\Delta S > 0$	$\Delta V > 0$
6	$\Delta G < 0$	$\Delta H < 0$	$\Delta S > 0$	$\Delta V < 0$

Select the set of thermodynamic parameters that best describes the system at room conditions

$H_2O_{(s)} \leftrightarrows H_2O_{(L)}$

	ΔG	ΔH	ΔS	ΔVolume
1	$\Delta G = 0$	$\Delta H > 0$	$\Delta S > 0$	$\Delta V > 0$
2	$\Delta G = 0$	$\Delta H > 0$	$\Delta S < 0$	$\Delta V = 0$
3	$\Delta G < 0$	$\Delta H > 0$	$\Delta S < 0$	$\Delta V < 0$
4	$\Delta G < 0$	$\Delta H > 0$	$\Delta S > 0$	$\Delta V < 0$
5	$\Delta G < 0$	$\Delta H < 0$	$\Delta S > 0$	$\Delta V > 0$
6	$\Delta G < 0$	$\Delta H < 0$	$\Delta S > 0$	$\Delta V < 0$

Consider the gas phase equilibrium
$2CO + O_2 \leftrightarrows 2CO_2$ at 25ºC

K = 11.1 Calculate ΔG

1. 500 kJ
2. 0.500 kJ
3. 5.96 kJ
4. 5960 kJ
5. −500 kJ
6. −0.500 kJ
7. −5.96 kJ
8. −5960 kJ

Consider the gas phase equilibrium

$2CO + O_2 \leftrightharpoons 2CO_2$ at 25ºC

K = 11.1 Calculate ΔG

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

$$\Delta G = -\left(0.00831 kJ / K\right)(298 K)(\ln 11.1)$$

1. 500 kJ
2. 0.500 kJ
3. 5.96 kJ
4. 5960 kJ
5. −500 kJ
6. −0.500 kJ
7. −5.96 kJ
8. −5960 kJ

Which apply to any reaction that proceeds spontaneously to form products from initial standard conditions.

1. $\Delta G < 0$
2. $K_{eq} > 1$
3. $\Delta H < 0$
4. $\Delta S > 0$

Which apply to any reaction that proceeds spontaneously to form products from initial standard conditions.

1. $\Delta G < 0$
   - because we know that if the reaction proceeds (spontaneous) it must have a negative ΔG.
2. $K_{eq} > 1$
   - because we know at standard conditions of 1 atm, 1M K would always = 1, so if the reaction proceeds K will end up greater than 1 since as the reaction proceeds products will increase and reactants will decrease resulting in K larger than 1.
3. $\Delta H < 0$
4. $\Delta S > 0$

Can every non spontaneous reaction, be made spontaneous by adjusting temperature?

1. yes
2. no
3. I don’t know, and I would just be guessing or following my neighbors, but I don’t really know how to analytically think through to an answer.

Can every non spontaneous reaction, be made spontaneous by adjusting temperature?

1. yes
2. no, remember: $\Delta G = \Delta H - T\Delta S$

- When ΔH is +, and ΔS is −, NO temperature will ever make the reaction spontaneous

- If ΔH is + and ΔS is +,
  - ✓ increasing the T will at some (even if theoretical) temp make $|T\Delta S| > |\Delta H|$ resulting in $\Delta G < 0$

- If ΔH is − and ΔS is −,
  - ✓ decreasing the T will at some temp make $|T\Delta S| < |\Delta H|$ resulting in $\Delta G < 0$

For a spontaneous reaction, what happens to the value of ΔG as a reaction proceeds?

1. gets more negative
2. gets less negative
3. stays the same

For a spontaneous reaction, what happens to the value of ΔG as a reaction proceeds?

1. gets more negative
2. gets less negative
3. stays the same

The reaction below is not spontaneous at room condition but becomes spontaneous at higher temperatures.

$2C_{(g)} \rightarrow A_{(g)} + 3B_{(g)}$

Which one of the following is true at 298 K (room temp)?

1. ΔG, ΔH, and ΔS are all positive
2. ΔG, ΔH, and ΔS are all negative
3. ΔG and ΔH are positive, but ΔS is negative
4. ΔG and ΔS are positive, but ΔH is negative
5. ΔG and ΔH are negative, but ΔS is positive
6. ΔG and ΔS are negative, but ΔH is positive
7. ΔG is positive, but we can not know about the sign of ΔS or ΔH
8. ΔG is negative, but we can not know about the sign of ΔS or ΔH

The reaction below is not spontaneous at standard conditions but becomes spontaneous at higher temperatures. $2C_{(g)} \rightarrow A_{(g)} + 3B_{(g)}$ Which of the following is true at 298 K?

1. ΔG, ΔH, and ΔS are all positive
    - at 298 K, not spontaneous means G +
    - when ΔS is positive, the |TΔS| factor will increase at higher temperatures and since the equation is, − TΔS, at some temp the |TΔS| factor will be greater than the |ΔH| and the value of ΔG will become negative.
2. ΔG, ΔH, and ΔS are all negative
3. ΔG and ΔH are positive, but ΔS is negative
4. ΔG and ΔS are positive, but ΔH is negative
5. ΔG and ΔH are negative, but ΔS is positive
6. ΔG and ΔS are negative, but ΔH is positive
7. ΔG is positive, but we can not know about the sign of ΔS or ΔH
8. ΔG is negative, but we can not know about the sign of ΔS or ΔH

Which parameters below correctly describe the condensation of water on the inside of your car windshield on a cold morning. *Select all that apply.*

into liquid or solid

1. $\Delta G < 0$
2. $\Delta H < 0$
3. $\Delta S < 0$
4. $\Delta V < 0$ V for volume of the water

The only reason we get condensation is because you are breathing out lots of water vapor.

Which parameters below correctly describe the condensation of water on the inside of your car windshield on a cold morning. *Select all that apply.*

1. $\Delta G < 0$
- indeed this is a spontaneous reaction, you've seen it happen as you are trying to see through the windshield while driving to school.
2. $\Delta H < 0$
- vaporization is endothermic, condensation is exothermic
3. $\Delta S < 0$
- liquid has less entropy than the gas
4. $\Delta V < 0$
- the liquid takes up less space than its gas

ΔH for the reaction below is negative

$N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)} \quad \Delta H = -97 kJ$

Which is larger in magnitude, the bond enthalpy of the reactants or products?

1. reactants
2. products
3. depends on other factors and cannot be determined with the given information

ΔH for the reaction below is negative

$N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)} \quad \Delta H = -97 kJ$

Which is larger, the bond dissociation value of the reactants or products?

1. reactants
2. products

- Without looking up and dissociation values, we know that bond forming, exothermic must be greater than bond breaking in order for the ΔH of the reaction to be negative, exothermic.

3. depends on other factors and cannot be determined with the given information

Consider the disorder of the following reactions and select the choice for which the sign of ΔS is CORRECT.

Select all that apply.

1. $H_2O_{(s)} \rightarrow H_2O_{(L)}$ ΔS −
2. $Ag^+_{(aq)} + Cl^-_{(aq)} \rightarrow AgCl_{(s)}$ ΔS −
3. $CaO_{(s)} + CO_{2(g)} \rightarrow CaCO_{3(s)}$ ΔS −
4. $2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)}$ ΔS +
5. $2Fe_2O_{3(s)} \rightarrow 4Fe_{(s)} + 3O_{2(g)}$ ΔS +

Consider the disorder of the following reactions and select the choice for which the sign of ΔS is CORRECT.

Select all that apply.

1. $H_2O_{(s)} \rightarrow H_2O_{(L)}$ $\Delta S -$
2. $Ag^+_{(aq)} + Cl^-_{(aq)} \rightarrow AgCl_{(s)}$ $\Delta S -$
3. $CaO_{(s)} + CO_{2(g)} \rightarrow CaCO_{3(s)}$ $\Delta S -$
4. $2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)}$ $\Delta S +$
5. $2Fe_2O_{3(s)} \rightarrow 4Fe_{(s)} + 3O_{2(g)}$ $\Delta S +$

Choose the pair of samples of matter that correctly compares their entropy values.

Select all that apply.

	The entropy of	*is*	*the entropy of*
1	$HCl_{(g)}$ at 25º	<	$Na_2SO_{4(s)}$ at 25º
2	$H_2O_{(L)}$ at 25º	<	$H_2O_{(L)}$ at 50º
3	$Ne_{(g)}$ at 25º	<	$Ar_{(g)}$ at 25º
4	$NO_{2(g)}$ at STP	<	$N_2O_{4(g)}$ at STP
5	$N_{2(g)} + 3H_{2(g)}$ at STP	<	$2NH_{3(g)}$ at STP

Choose the pair of samples of matter that correctly compares their entropy values.

Select all that apply.

	The entropy of	*is*	*the entropy of*
1	$HCl_{(g)}$ at 25º	<	$Na_2SO_{4(s)}$ at 25º
2	$H_2O_{(L)}$ at 25º	<	$H_2O_{(L)}$ at 50º
3	$Ne_{(g)}$ at 25º	<	$Ar_{(g)}$ at 25º
4	$NO_{2(g)}$ at STP	<	$N_2O_{4(g)}$ at STP
5	$N_{2(g)} + 3H_{2(g)}$ at STP	<	$2NH_{3(g)}$ at STP

Select the thermodynamic quantity below that is negative for any exothermic reaction.

Select as many as apply.

1. K_{eq}
2. ΔG
3. ΔH
4. ΔS
5. ΔV (volume)

Select the thermodynamic quantity below that is negative for any exothermic reaction.

Select as many as apply.

1. K_{eq}
2. ΔG
3. ΔH
4. ΔS
5. ΔV (volume)

Select the thermodynamic quantity below that is always positive for all spontaneous reactions.

Select as many as apply.

1. K_{eq}
2. ΔG
3. ΔH
4. ΔS
5. ΔV (volume)

Select the thermodynamic quantity below that is always positive for all spontaneous reactions.

Select as many as apply.

1. K_{eq}
- In fact K is positive for ALL reactions.
2. ΔG (must be negative)
3. ΔH (depends...)
4. ΔS (depends...)
5. ΔV (volume) (depends...)

Select the thermodynamic quantity below that can be negative for spontaneous reactions.

Select as many as apply.

1. K_{eq}
2. ΔG
3. ΔH
4. ΔS
5. ΔV (volume)

Select the thermodynamic quantity below that can be negative for spontaneous reactions.

Select as many as apply.

1. K_{eq}
   - K_{eq} is never a negative value
2. ΔG (must be)
3. ΔH
4. ΔS
5. ΔV (volume)

ΔG_f^o for NO = +87 kJ/mol

ΔG_f^o for NO_2 = +52 kJ/mol

Select the true statement(s) below.

1. The formation of NO will occur faster than the formation of NO_2.
2. NO_2 is more stable than NO.
3. $NO + \frac{1}{2}O_2 \rightarrow NO_2$ is a spontaneous reaction.
4. The formation of NO_2 is spontaneous at all reaction temperatures.
5. $NO \rightarrow N_2 + \frac{1}{2}O_2$ is spontaneous

ΔG_f^o for NO = +87 kJ/mol
ΔG_f^o for NO_2 = +52 kJ/mol
Select the true statement(s) below.

1. The formation of NO will occur faster than the formation of NO_2.
2. NO_2 is more stable than NO.
3. $NO + \frac{1}{2}O_2 \rightarrow NO_2$ is a spontaneous reaction.
4. The formation of NO_2 is spontaneous at all reaction temperatures.
5. $NO \rightarrow N_2 + \frac{1}{2}O_2$ is spontaneous

When two solutions are combined and a precipitate forms, the solution cools. Which describes the value of ΔG, and its components?

1. $\Delta G < 0$, $|\Delta H| > |T\Delta S|$
2. $\Delta G < 0$, $|\Delta H| < |T\Delta S|$
3. $\Delta G > 0$, $|\Delta H| > |T\Delta S|$
4. $\Delta G > 0$, $|\Delta H| < |T\Delta S|$
5. $\Delta G = 0$, $|T\Delta S| = |\Delta H|$

When two solutions are combined and a precipitate forms while the solution cools. Which describes the value of ΔG, and its components?

1. $\Delta G < 0$, $|\Delta H| > |T\Delta S|$
2. $\Delta G < 0$, $|\Delta H| < |T\Delta S|$
   - Since we know that the solution cools, we know that ΔH is positive, and since that is an unfavorable factor the S must be driving the reaction, thus ΔS must be positive.
   - although it is completely counter intuitive, the driving force for this reaction *must* be an increase in entropy,
   - and for the reaction to be spontaneous ($\Delta G<0$), the $|T\Delta S|$ factor must be larger than the $|\Delta H|$ factor.
3. $\Delta G > 0$, $|\Delta H| > |T\Delta S|$
4. $\Delta G > 0$, $|\Delta H| < |T\Delta S|$
5. $\Delta G = 0$, $|T\Delta S| = |\Delta H|$

That’s all for now…

Calculating ΔS

for phase changes

At what temperature is this process at equilibrium? $H_2O_{(g)} \leftrightharpoons H_2O_{(L)}$

- What temperature does ice melt?
- What temperature does water freeze?
- At 0ºC, water can do either, depending on whether or not energy is entering or exiting the system.
- If no heat is transfering, the system is at equilibrium

Using Boiling and Melting points to calculate ΔS

- When a substance is at its *normal* boiling or melting temperature it is at *equilibrium*.
- And at equilibrium $\Delta G = 0$
- Since $\Delta G = \Delta H^\circ - T\Delta S^\circ$
- $T\Delta S^\circ = \Delta H^\circ$
- So the ΔS of melting or boiling = $\Delta H/T$
  - ✓ This is one method of calculating entropy for some substances.

The molar heat of fusion, ΔH_{fus}, for water is 6.01 kJ mol^{-1}. Which expression gives the molar entropy of fusion, ΔS_{fus}, in kJ K^{-1} mol^{-1} for ice at its *normal* melting point?

1. $\Delta S_{fus} = 6.01 \times 4.18$
2. $\Delta S_{fus} = 6.01 \times 273$
3. $\Delta S_{fus} = 6.01 \times 298$
4. $\Delta S_{fus} = \dfrac{6.01}{273}$
5. $\Delta S_{fus} = \dfrac{6.01}{298}$

The molar heat of fusion, ΔH_{fus}, for water is 6.01 kJ mol^{-1}. Which expression gives the molar entropy of fusion, ΔS_{fus}, in kJ K^{-1} mol^{-1} for ice at its *normal* melting point?

1. $\Delta S_{fus} = 6.01 \times 4.18$
2. $\Delta S_{fus} = 6.01 \times 273$
3. $\Delta S_{fus} = 6.01 \times 298$
4. $\Delta S_{fus} = \dfrac{6.01}{273}$
5. $\Delta S_{fus} = \dfrac{6.01}{298}$

Yankee Swap Variations - vote 1, 2, or 3

- Version 1: The person who picks the first gift opens it and shows it to everyone. Then the number two participant picks a gift and chooses to either unwrap it or swap it for an unwrapped gift. If the gift is swapped, the person who had their gift taken from them gets to unwrap the new gift. The game goes on until everyone has had their chance. Then the number one swapper can swap their gift with any of the unwrapped gifts.

- Version 2 (the cascade): The person who picks the first gift opens it and shows it to everyone. Then the number two participant picks a wrapped gift, opens the gift, and can keep the gift or swap for an unwrapped gift. That person who’s gift has just been been swapped can exchange for another unwrapped gift that has not been taken during that turn. The turn is over when a person chooses to keep the gift or all of the gifts have been swapped in that turn. Then the number one swapper can swap their gift with any of the unwrapped gifts.

- Version 3 (the blind cascade): The person who picks the first gift opens it and shows it to everyone. Then the number two participant chooses to pick a wrapped gift OR take an unwrapped gift from someone. That person who’s gift has been taken can take either an unwrapped gift, or choose a wrapped gift from the pile. The turn is over when a wrapped gift is selected. The stealing of unwrapped gifts can go on in any one “turn” until someone chooses a wrapped gift. (An unwrapped gift can only be taken once in any “turn.”) Then the number one swapper can swap their gift with any of the unwrapped gifts.