

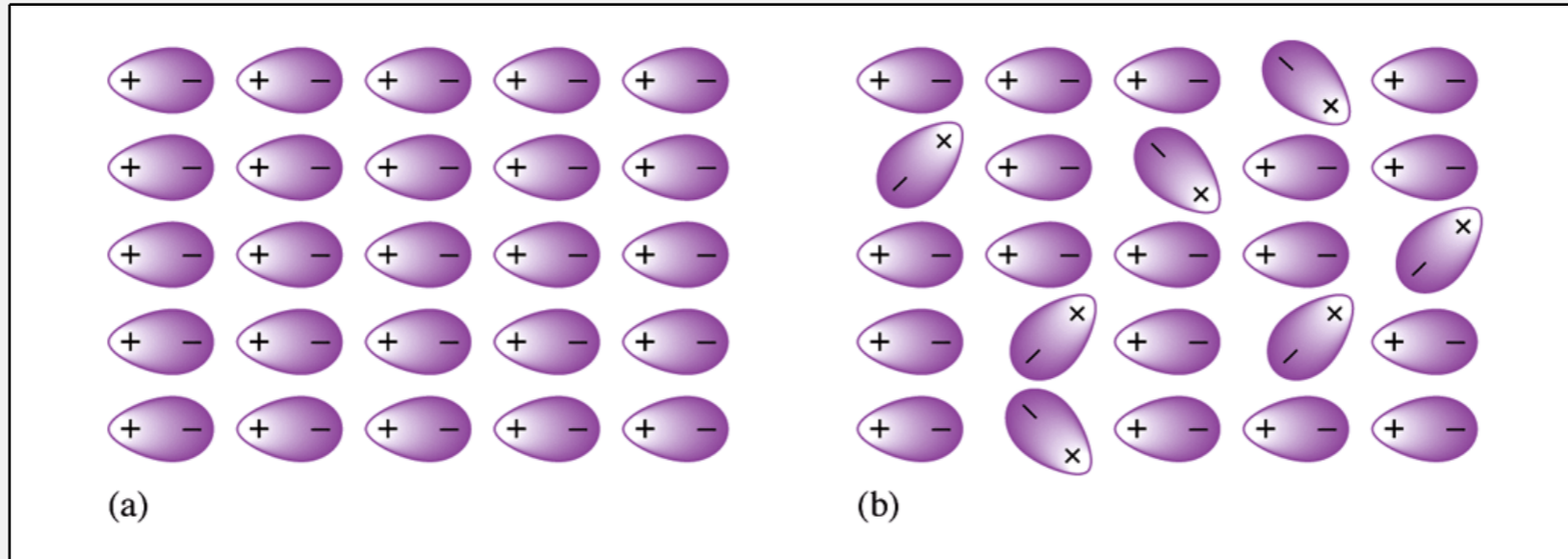
# **Chapter 16: Spontaneity, Entropy, and Free Energy**

# Entropy (S)

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Measure of **randomness** or **disorder** in a system  
(this will all tie in to enthalpy in the next couple days)

- The greater the **disorder**, the greater the **entropy**
- Zero entropy is a solid crystal at 0 K
- Therefore **all** things have **some** positive entropy associated with them
- We will often use **standard** entropies ( $S^\circ$ ) which are the entropies at 25°C



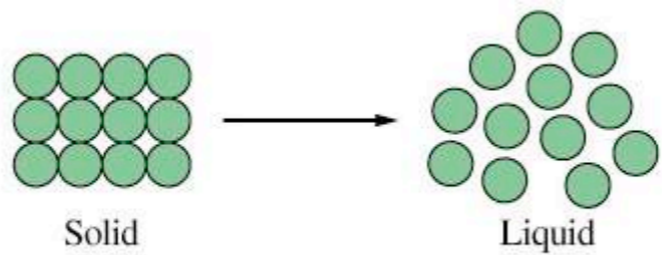
(a) A perfect crystal of hydrogen chloride at 0 K.

(b) As the temperature rises above 0 K, lattice vibrations allow some dipoles to change their orientations, producing some disorder and an increase in entropy.

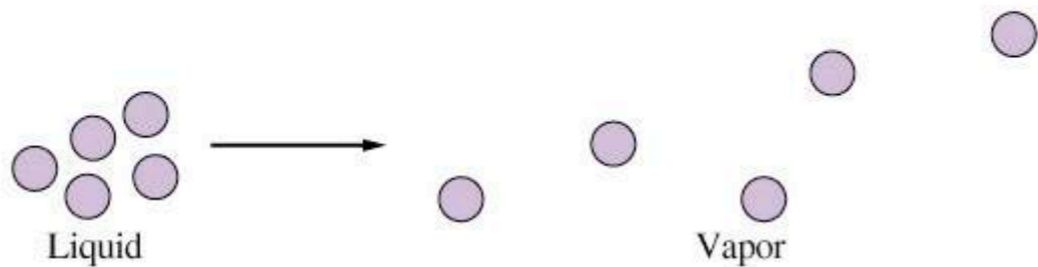
# Entropy Rules of Thumb

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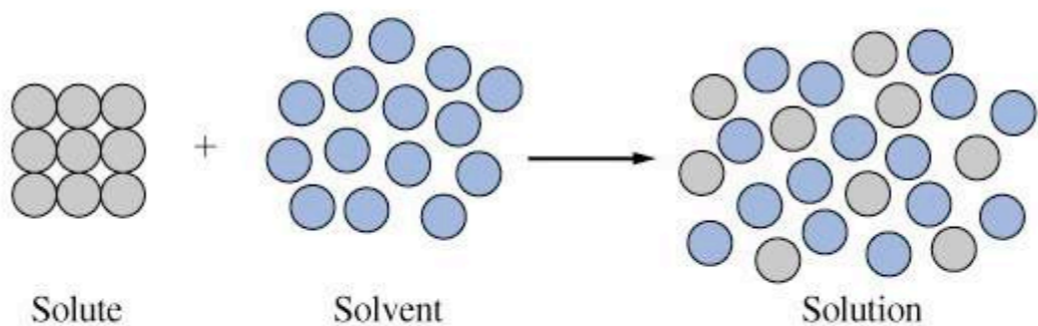
- liquids  $>$  solids
- gases  $>$  liquids
- particles in soln  $>$  solids
- 2 moles  $>$  1 mole



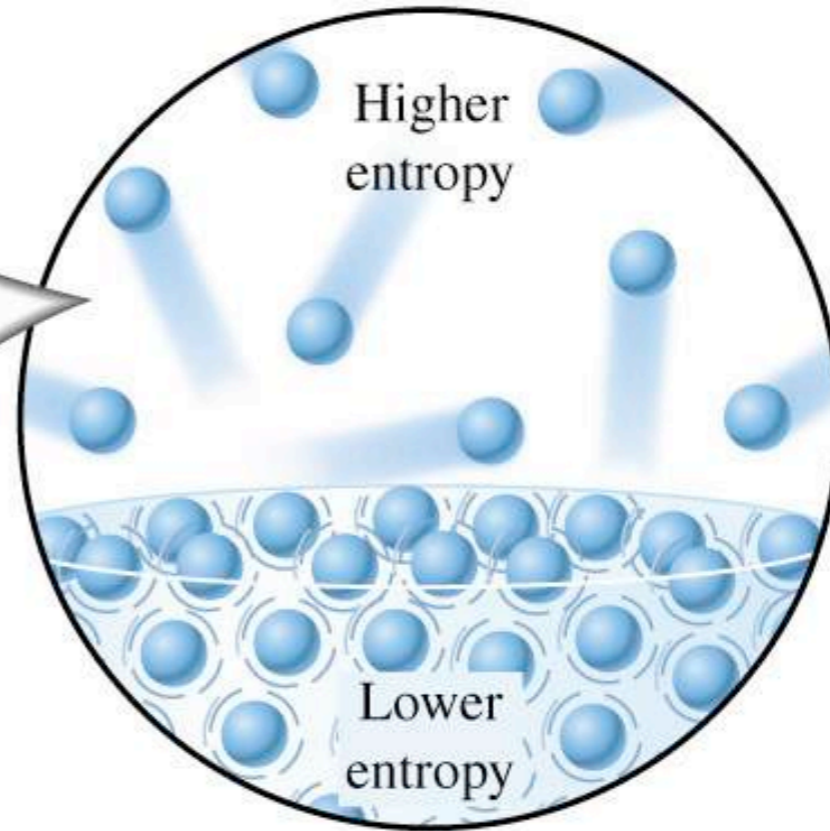
(a) Melting:  $S_{\text{liquid}} > S_{\text{solid}}$

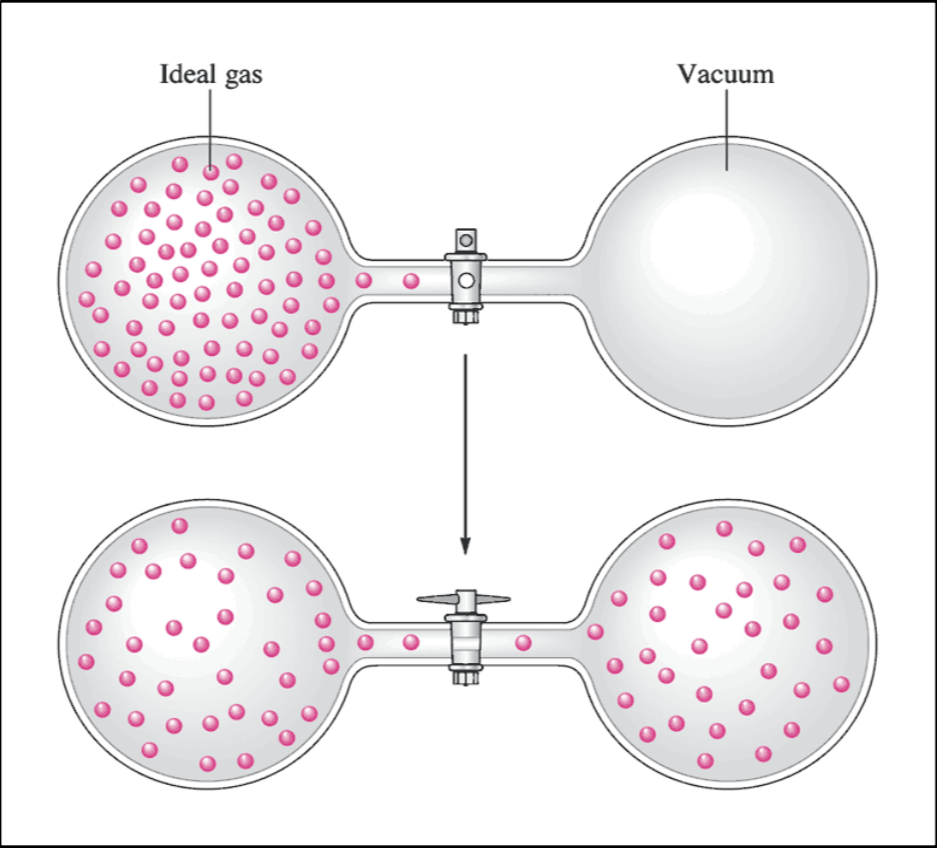


(b) Vaporization:  $S_{\text{vapor}} > S_{\text{liquid}}$



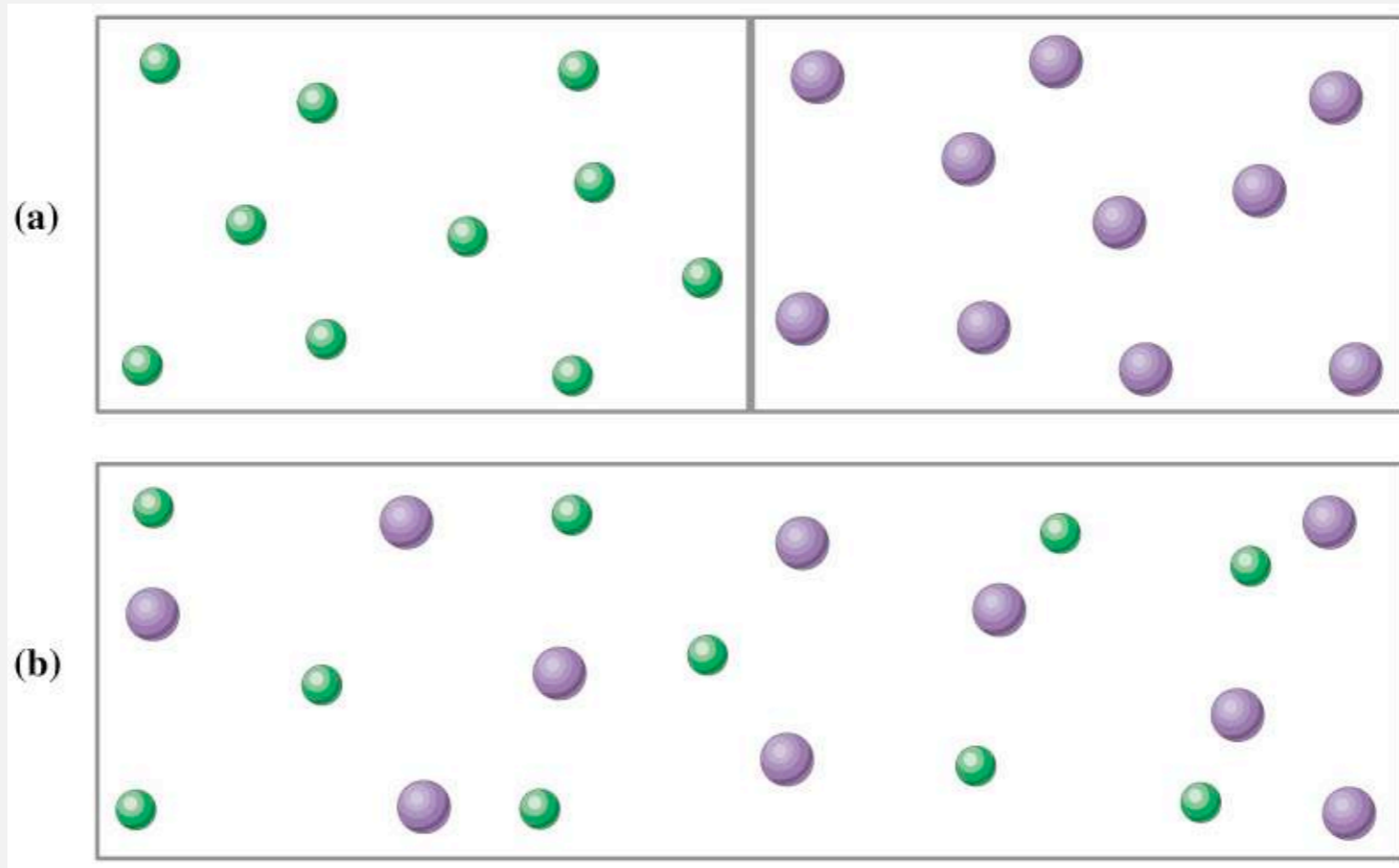
(c) Dissolving:  $S_{\text{soln}} > (S_{\text{solvent}} + S_{\text{solute}})$



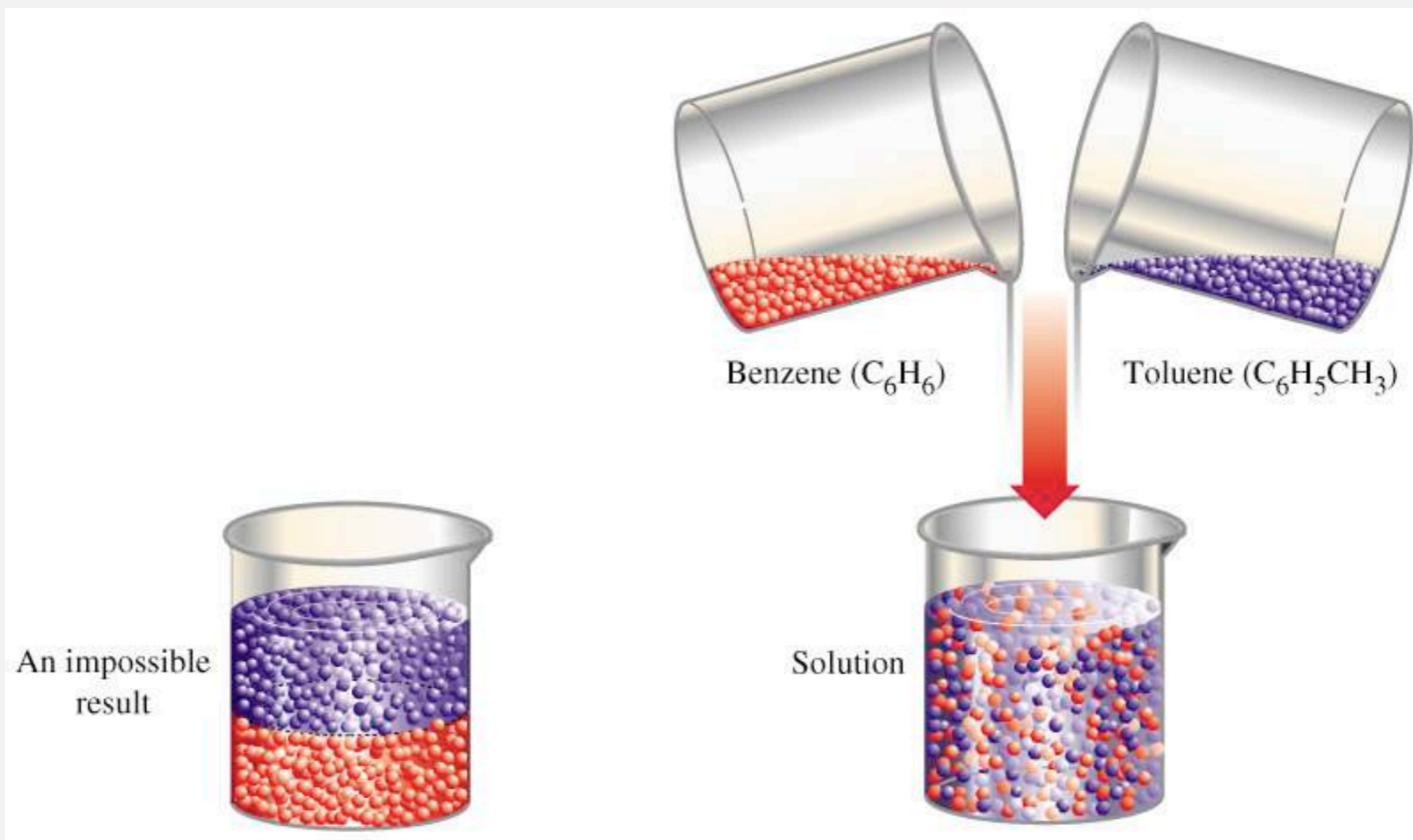


which has greater entropy???

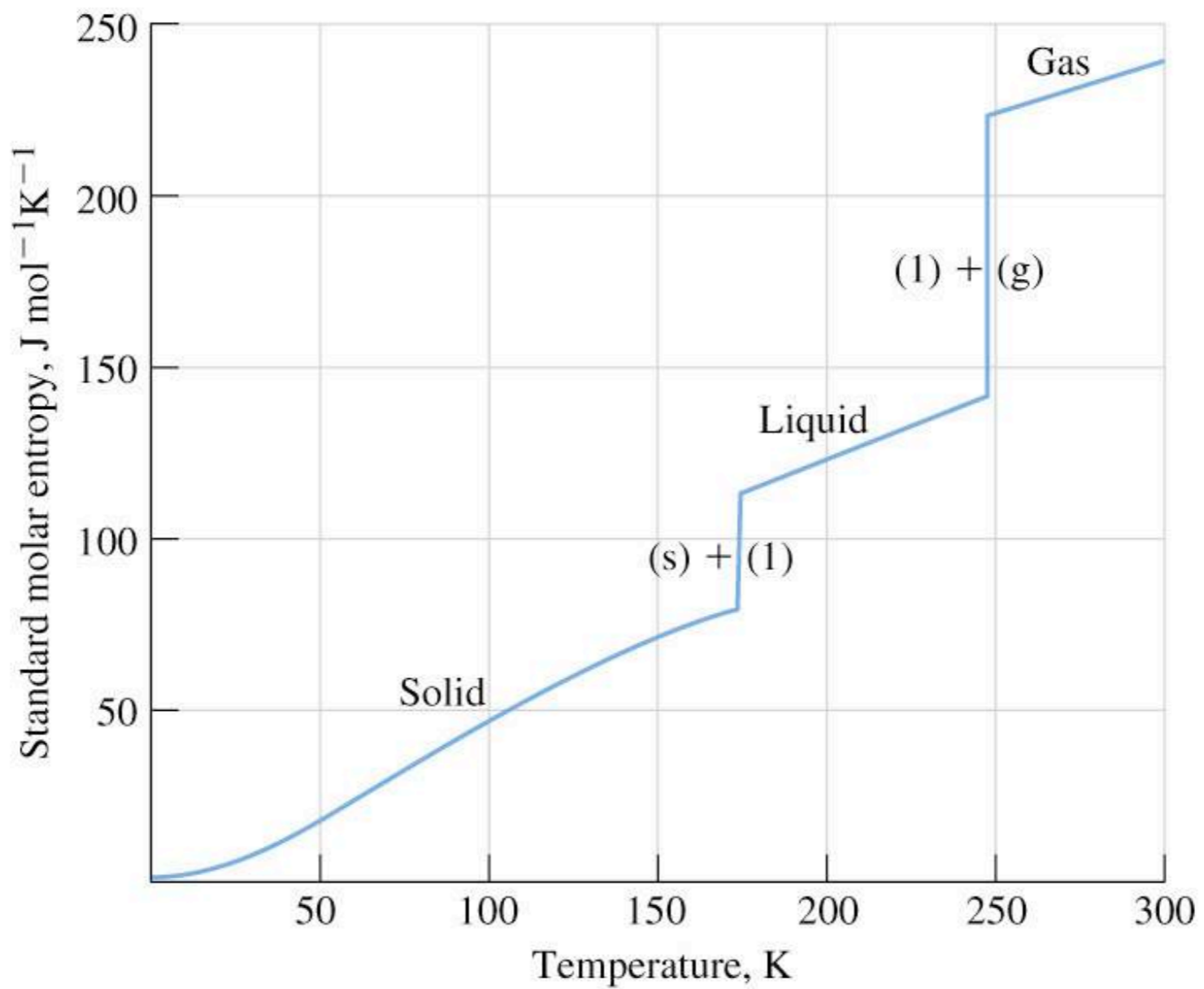




which has greater entropy???



which has greater entropy???



which **phase change** has greatest entropy change? why?

For which process is  $\Delta S$  negative?

- 1) Evaporation of 1 mol of  $\text{CCl}_4(\text{l})$
- 2) Mixing 5 mL ethanol with 25 mL water
- 3) Compressing 1 mol Ne at constant temperature
- 4) Raising the temperature of 100 g Cu from 275 K to 295 K
- 5) Grinding a large crystal of KCl to powder

question

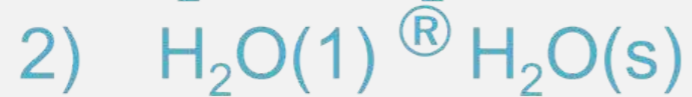
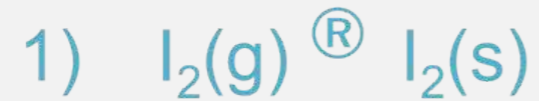
3) Compressing 1 mol Ne at constant temperature

Section 16.1 Spontaneous Processes and Entropy (p. 786)

The Ne atoms have less space to move, which decreases their randomness.

answer

In which reaction is  $\Delta S^\circ$  expected to be positive?



5) None of these

question

5) None of these

Section 16.1 Spontaneous Processes and Entropy (p. 786)

Each of these reactions produces either a solid, liquid or fewer gas molecules.

answer

# QUESTION

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Of the following, which would have a negative entropy change?

1. A salt crystal dissolves in water.
2. Dry ice (solid  $\text{CO}_2$ ) sublimates at room temperature.
3. Individual amino acids bond together to make a protein.
4. Liquid gasoline combusts to form  $\text{CO}_2$  and  $\text{H}_2\text{O}$  gas molecules.



**Choice 3** shows a change that decreases entropy. Individual amino acid molecules can be arranged in a variety of changing positions due to their independence. However, once bonded into a protein there is a set organized sequence. This would indicate a decrease (negative) in entropy.

## Section 16.1: Spontaneous Processes and Entropy



answer

eocs

Ch. 16 # 24,25,33,34

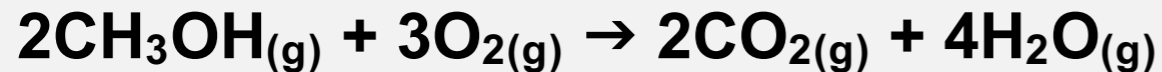
# Entropy Change

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- ***How much*** the entropy changed in a reaction is the difference between the  $S$  of the products and the  $S$  of the reactants

- **$\Delta S^\circ = \sum S^\circ \text{ products} - \sum S^\circ \text{ reactants}$**

- Calculate  $\Delta S^\circ$  of the following reaction:



$\text{CO}_{2(g)}$	214	J/K · mol
$\text{CH}_3\text{OH}_{(g)}$	240	J/K · mol
$\text{CH}_3\text{OH}_{(l)}$	127	J/K · mol
$\text{O}_{2(g)}$	205	J/K · mol
$\text{H}_2\text{O}_{(g)}$	189	J/K · mol
$\text{H}_2\text{O}_{(l)}$	70	J/K · mol

# Gibbs Free Energy

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G is a measurement of the **spontaneity** of a process (H and S play a big role here)...  
i.e. *does it happen by itself without intervention?*

- Does **not** tell you how **fast** it happens!!!  
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Does **not** tell you how **fast** it happens!!! (that's **kinetics**)
- For a given reaction:
- If  $\Delta G$  is **negative**, the rxn is **spontaneous**
  - If  $\Delta G$  is **positive**, the rxn is **not spontaneous** (we need to force it to happen)
  - If  $\Delta G = 0$ , the rxn is at **equilibrium**

# Free Energy Change

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- **One** way to be found is just like  $\Delta S$  and  $\Delta H$ ...
- Use the  $\Delta G_f^\circ$  values (std free energy of formation) for the reactants and products
  - **$\Delta G^\circ = \sum G_f^\circ \text{ products} - \sum G_f^\circ \text{ reactants}$**
- Exercise 16.11 (pg. 769)
- Exercise 16.12 (pg. 770)

eocs

Ch 16 # 51,53,55

## $\Delta G$ , $\Delta H$ , and $\Delta S$

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- whether something is spontaneous or not, can be observed in ***another*** equation
- nature loves **low energy** (decreasing enthalpy)
- nature loves **high disorder** (increasing entropy)
- the equation that combines these two is:

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

- temp is in K...



**TABLE 20.1 Criteria for Spontaneous Change:  $\Delta G = \Delta H - T \Delta S$**

Case	$\Delta H$	$\Delta S$	$\Delta G$	Result	Example
1	-	+	-	spontaneous at all temp	$2 \text{ N}_2\text{O}(\text{g}) \longrightarrow 2 \text{ N}_2(\text{g}) + \text{ O}_2(\text{g})$
2	-	-	{ - + }	{ spontaneous at low temp nonspontaneous at high temp }	$\text{ H}_2\text{O}(\text{l}) \longrightarrow \text{ H}_2\text{O}(\text{s})$
3	+	+	{ + - }	{ nonspontaneous at low temp spontaneous at high temp }	$2 \text{ NH}_3(\text{g}) \longrightarrow \text{ N}_2(\text{g}) + 3 \text{ H}_2(\text{g})$
4	+	-	+	nonspontaneous at all temp	$3 \text{ O}_2(\text{g}) \longrightarrow 2 \text{ O}_3(\text{g})$

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

- Exercise 16.9

- Calculate  $\Delta H^\circ$ ,  $\Delta S^\circ$ , and  $\Delta G^\circ$  for the following reaction. (Careful of KJ/J conversions)



Substance	$\Delta H^\circ_f$ (kJ/mol)	$\Delta s^\circ_f$ (J/K·mol)
$\text{SO}_{2(g)}$	-297	248
$\text{SO}_{3(g)}$	-396	257
$\text{O}_{2(g)}$	0	205

eoc

16.45 (show work!)

## [The Equilibrium Constant]REMEMBER THIS?

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- When a reaction happens, it doesn't mean it has to go to full products with no reactants left at all; it stops at a place we call **equilibrium**
- There are some products and some reactants at the “end” of the reaction
- This all gives us an **equilibrium expression...**

# [The Equilibrium Constant]

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- For this reaction: **aA + bB = cC + dD**, the expression is...

- **$K_{eq} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$**

- *The [X] critters are the concentrations of these guys at equilibrium (or partial pressures!!!)*
- *Products are above Bob, reactants below*
- *The coefficients become exponents*
- *Solids and pure liquids are not invited!!!*

# [Reaction Quotient]

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- what does this look like?

- $Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$

- This is the **reaction quotient**, i.e. where it is at a particular time in a reaction, *not necessarily equilibrium*
- if Q is **less** than  $K_{eq}$ , the reaction is a go, it will form products
- if Q is **greater** than  $K_{eq}$ , the reaction goes backwards, making reactants
- if  $Q = K$ , we have equilibrium!

## $\Delta G$ and $\Delta G^\circ$

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- $\Delta G^\circ$  is the free energy change when everything is in its standard state concentration (1 molar, 1 atmosphere, etc.)
- *but what if the players aren't in their std state concentrations??? What is  $\Delta G$  for that reaction???*

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

- $\Delta G$  = free energy change under given initial conditions (J)

- $\Delta G^\circ$  = standard free energy change (J)

- R = gas constant (here 8.31 J/mol•K)

- T = absolute temperature

- Q = the reaction quotient for the given initial conditions



# example

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- 16.14 (821)

eocs

16.59 (show work)

# Standard Free Energy Change and the Equilibrium Constant

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- At equilibrium  $\Delta G = 0$  **AND**  $Q = K$ , OK?
- If so, then at equilibrium, when all the reactants and products are happiest, do you see that  $\Delta G = \Delta G^\circ + RT \ln Q$  becomes...

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

- if  $\Delta G^\circ$  is **negative**,  $K$  must be greater than 1: **products** are favored @ eq
- if  $\Delta G^\circ$  is **positive**,  $K$  must be less than 1: **reactants** are favored @ eq

# example

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- 16.15 (822)

eoc

16.61, 62 (show work!)