spontaneous – product favored nonspontaneous – reactant favored

combustion of propane	spontaneous and exothermic		
NaOH $(aq)$ + HCl $(aq)$	spontaneous and exothermic		
$\mathbf{H}_{2}\mathbf{O}_{(l)}  \mathbf{H}_{2(g)} + \frac{1}{2}\mathbf{O}_{2(g)}$	non-spontaneous		
$\mathbf{H}_{2(g)} + \frac{1_{2}}{\mathbf{O}_{2(g)}} \rightarrow \mathbf{H}_{2}\mathbf{O}_{(l)}$	spontaneous and exothermic		

Many spontaneous reactions are exothermic. But that's not all there is to it.

- 2 factors that favor spontaneity
  - a) heat is released (exothermic)
  - b) increase in disorder

 $2^{nd}$  law of thermodynamics – in spontaneous changes, universe tends toward state of greater disorder

<u>entropy</u> (S) – a measure of the disorder of the system

analogies: hair spray comes out of can, dorm room gets messy during finals

the more ways an event can happen, the more probable that event is

 $\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} > 0$ 

ex. some physical changes which increase entropy (disorder)

- 1) mixing of pure substances (Fig. 15-12)
- 2) some phase changes (ex. from  $s \rightarrow 1 \text{ or } l \rightarrow g$ )
- 3) increase in temperature (kin. E of gas)
- 4) increase in volume

 $Ba(OH)_2 \bullet 8H_2O(s) + 2NH_4SCN(s) \rightarrow Ba(SCN)_2(aq) + 2NH_3(l) + 10H_2O(l)$ 

This is an acid/base reaction  $(NH_4^+ is the acid)$ 

It is endothermic (heat consumed) but spontaneous. Why does it happen?

Entropy of system must increase

solids	$\rightarrow$	liquids and solutions	
3 mole reactants	$\rightarrow$	14 mole products	

ex. some chemical changes which increase entropy

- 1) # particles (moles) increase (demo)
- 2) # moles of gas increase

 $C_{8}H_{18}(g) + 5O_{2}(g) \rightarrow 9H_{2}O(l) + 8CO_{2}(g)$ 6 moles gas  $\rightarrow$  8 moles gas

$C_{3}H_{8}(g) +$	$5O_{2}(g)$	$\rightarrow$	$4H_2O(l)$ +	$3\mathrm{CO}_{2}\left(g\right)$
6 moles gas		$\rightarrow$	3 moles gas	

spontaneous reactions can

- be exothermic or
  cause increase in entropy of system or
- 3) both #1 & #2

 $\Delta S_{system}$  affects  $\Delta E_{system}$ 

Can we quantify entropy (like we quantified heat earlier in this chapter)?

<u>absolute standard molar entropy</u> – (appendix K) quantifies disorder in a substance at 298 K. +#

 $\frac{3^{rd} \text{ law of thermodynamics}}{(\text{ordered}) \text{ at } 0 \text{ K has absolute } S = 0.$ 

Note -H and E we don't have an absolute scale (we measure  $\Delta$ ). S does.

 $\Delta S^{o}_{rxn} = \Sigma n S^{o}_{prod} - \Sigma n S^{o}_{react}$ 

## <u>Gibbs free energy</u> (G) – amount of E available for system to do *useful* work (at constant T, <u>P</u>)

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

## Quiz #1

Write name, SID #, and Quiz # on paper – everyone has their own Work in groups – turn your papers in together

For each of the following processes, tell whether the entropy of the system increases, decreases, or stays the same:

- 1) freezing one mole of water to ice at 0°C
- 2) a building collapses
- 3) silver sulfate [Ag<sub>2</sub>SO<sub>4</sub>] precipitates from a solution containing silver ions and sulfate ions.
- 4) 35 pennies are taken out of bag and placed on table, heads up.