#### A. Second Law (Review statements summarized on web page)

Entropy, S a measure of disorder

$$dS = \frac{dq_{rev}}{T} \qquad \frac{Energy}{Temperature}$$

 $\Delta S_{\text{Universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$  Direction of spontaneous change.

# **B. Third Law** $\lim_{T \to 0} S(\text{pure crystalline substance}) = 0$

The entropy (disorder) of a pure crystalline substance goes to zero at zero Kelvin.

There is an absolute zero for the entropy of a substance (NOT TRUE FOR ENERGY).

Can define Absolute Entropy for any substance at given temperature.

Get from heat capacity vs temperature measurements.

Compare  $S^0$  solid, liquid, gas, and as temperature increases

#### C. Physical Changes

Heat/Cool substance	$\Delta S = nC_p ln(T_2/T_1)$	(HEAT CAPACITY INDEPENDENT OF TEMP)
Phase Change	$\Delta S_{phase} = \Delta H_{phase} / T_{phase}$	

Equilibrium process if done at temperature of phase change (NOTE: *NOT STANDARD TEMPERATURE*). Compare  $\Delta S_{phase}$  for melting, boiling, subliming

## **D.** Chemical Reaction $\Delta S^0_{rxn} = \sum n S^0(products) - \sum n S^0(reactants)$

Standard Absolute Entropies listed in thermodynamic tables.

F.	Surroundings	$\Delta S_{surroundings} = -\Delta H/T$	(CONSTANT PRESSURE AND TEMPERATURE)
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**E.** Gibbs Free Energy Derived energy from Second Law  $G \equiv H - TS$ 

 $\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings}$  $\Delta S_{system} \text{ from C or D above.} \qquad ... \qquad \Delta S_{surroundings} = -\Delta H/T$  $\Delta S_{universe} = \Delta S - \Delta H/T > 0 \qquad SPONTANEOUS (CONSTANT T & P)$ Multiply through by (-T)  $-T\Delta S_{universe} = \Delta H - T\Delta S = \Delta G \qquad GIBBS FREE ENERGY$ 

Tells direction of spontaneous change at constant T & P We can show that  $\Delta G = W(nonexpansion)$  Energy available to do non-expansion work.

$\Delta G = \Delta H - T \Delta S$	GIBBS - HELMHOLTZ EQUATION
$\Delta G < 0$	Spontaneous
$\Delta G = 0$	Equilibrium
$\Delta G > 0$	NOT Spontaneous> Spontaneous reverse direction

### **F.** Standard Gibbs Free Energy of reaction $\Delta G^{0}_{rxn}$

From Standard Gibbs Free Energies of Formation  $\Delta G^{0}_{rxn} = \sum n \Delta G^{0}_{f}(products) - \sum n \Delta G^{0}_{f}(reactants)$ 

From Standard Enthalpies of Formation and Standard Absolute Entropies  $\Delta G^{0}_{rxn} = \Delta H^{0}_{rxn} - T\Delta S^{0}_{rxn}$ 

Tells how far toward products the system is at equilibrium  $\Delta G^{0}_{rxn} < 0$  PRODUCT FAVORED = SPONTANEOUS UNDER STANDARD STATE CONDITIONS  $\Delta G^{0}_{rxn} > 0$  REACTANT FAVORED =NOT SPONTANEOUS UNDER STANDARD STATE CONDITIONS

**G.** Interpreting  $\Delta G = \Delta H - T\Delta S$  CONSTANT TEMP & PRESSURE

 $\Delta H < 0$  Exothermic. Favorable (*why?*) *Enthalpy driven* 

 $\Delta S > 0$  Favorable (*why*?) *Entropy driven* 

 $\Delta n_{gas} > 0$  or more mixed up products

Four Cases						
Case	$\Delta H$	$\Delta S$	$\Delta \mathbf{G} = \Delta \mathbf{H} - \mathbf{T} \Delta \mathbf{S}$	Interpretation		
1.	-	+	– ALL TEMPS	SPONTANEOUS ALL TEMPS		
2.	-	-	<ul><li>LOW TEMP</li><li>HIGH TEMP</li></ul>	SPONTANEOUS AT LOW TEMP		
3.	+	+	+ LOW TEMP - HIGH TEMP	SPONTANEOUS AT HIGH TEMP		
4.	+	-	+ ALL TEMPS	NOT SPONTANEOUS ANY TEMP MUST BE DRIVEN BY EXTERNAL INFLUENCE		

For cases 2 & 3 - Temperature at which  $\Delta G$  changes sign:  $\Delta G = 0$   $T = (\Delta H) / (\Delta S)$  assuming  $\Delta H$  and  $\Delta S$  are independent of T