

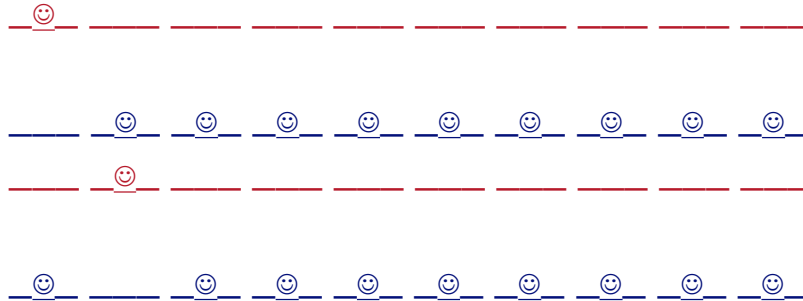
## Disorder and Entropy

- Suppose I have 10 particles that can be in one of two states—either the blue state or the red state. How many different ways can we arrange those particles among the states?
- All particles in the blue state: 1 configuration



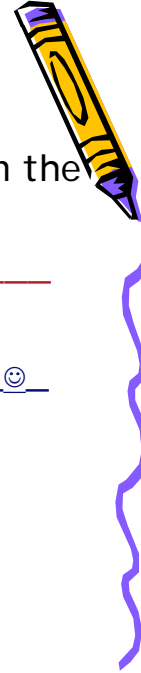
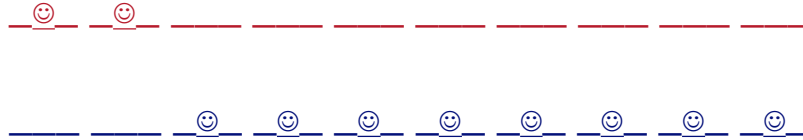
## Disorder and Entropy

- 9 particles in the blue state; 1 particle in the red state: 10 configurations



## Disorder and Entropy

- 8 particles in the blue state; 2 particles in the red state: 90 configurations



## Disorder and Entropy

- 7 particles in the blue state; 3 particles in the red state: 720 configurations



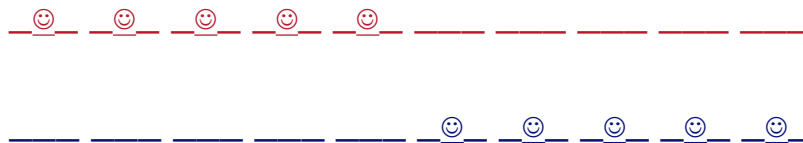
## Disorder and Entropy

- 6 particles in the blue state; 4 particles in the red state: 4320 configurations



## Disorder and Entropy

- 5 particles in the blue state; 5 particles in the red state: 21,600 configurations



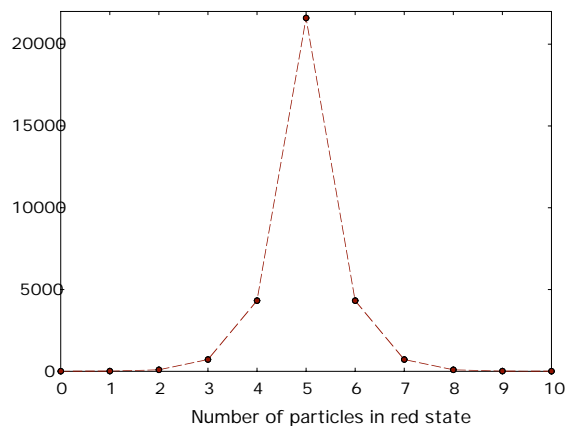
## Disorder and Entropy

- 4 particles in the blue state; 6 particles in the red state: 4320 configurations
- 3 particles in the blue state; 7 particles in the red state: 720 configurations
- 2 particles in the blue state; 8 particles in the red state: 90 configurations
- 1 particle in the blue state; 9 particles in the red state: 10 configurations
- 0 particles in the blue state; 10 particles in the red state: 1 configuration



## Disorder and Entropy

- Which configuration of particles will have the highest probability of being observed?



## Disorder and Entropy

- The most probable configuration is that with the highest level of disorder
  - The particles are spread between as many different states as possible
- *Entropy* is a measure of the amount of disorder in a system
- The 2<sup>nd</sup> Law of Thermodynamics states that entropy should be maximized—system contains the highest degree of disorder possible



## Disorder and Entropy

- This principle applies to a number of common systems:  
Putting ice in a warm drink:
  - Energetically, there is no reason why heat cannot flow from the solid into the liquid making the drink warmer and the ice colder
  - This would concentrate energy in the system, and not spread it out as much as possible
  - Entropy and the 2<sup>nd</sup> Law mandates that heat flow from hot to cold

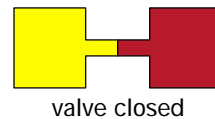


## Disorder and Entropy

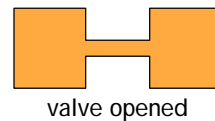
- This principle applies to a number of common systems:

Mixing of two gases at the same pressure:

- When the valve separating the gases is opened, the gases mix until they are equally dispersed throughout the container



- If there is no attraction between gases, there is no energetic reason



for mixing

- Mixing is consequence of 2<sup>nd</sup> Law and maximum entropy

## Entropy

- The change in entropy of a system,  $\Delta S$ , is related to its heat content

$$\Delta S = S_{final} - S_{initial} = \frac{q_{rev}}{T}$$

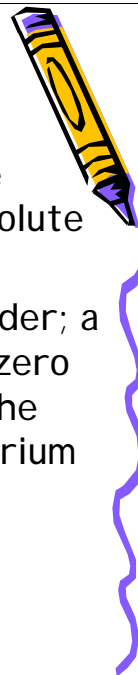
$q_{rev}$  is the heat exchanged between the system and its surrounding during a reversible process

Reversible processes are those in which changes occur in infinitesimally small steps during an infinitely long time



## Entropy

- Entropy is the only thermodynamic state function that can be measured on an absolute scale:
- Remember entropy is a measure of disorder; a pure solid at a temperature of absolute zero has no kinetic energy ( $E_T = 3/2 RT$ ), so the molecules do not move from their equilibrium positions
- This system has no disorder, so  $S = 0$



## Entropy

- The entropy of a solid is lower than that of a liquid which is lower than that of a gas

$$S_{\text{H}_2\text{O}(s)} = 49.5 \text{ J/mol}\cdot\text{K}$$

$$S_{\text{H}_2\text{O}(l)} = 70.0 \text{ J/mol}\cdot\text{K}$$

$$S_{\text{H}_2\text{O}(g)} = 188.8 \text{ J/mol}\cdot\text{K}$$

- Solids are more ordered than liquids
- Liquids are more ordered than gases



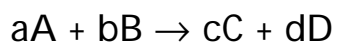
## Entropy

- Entropy usually increases upon dissolution of a solute in a solvent
- The solute is more disordered in solution than in the solid phase
- Solutions of some salts have decreased entropy upon dissolution because the ions are strongly hydrated—the water solvent molecules becomes more ordered in the region surrounding the ion



## Entropy

- We can calculate entropy using Hess's Law



$$\Delta S_{\text{rxn}} = (c \cdot S_C + d \cdot S_D) - (a \cdot S_A + b \cdot S_B)$$

In general:

$$\Delta S_{\text{rxn}} = \sum_{\text{prods}} n_i \cdot S_i - \sum_{\text{reacts}} n_i \cdot S_i$$

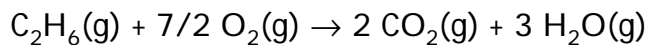
where  $S_i$  is the entropy of the compound and  $n_i$  is its stoichiometric coefficient





# Entropy

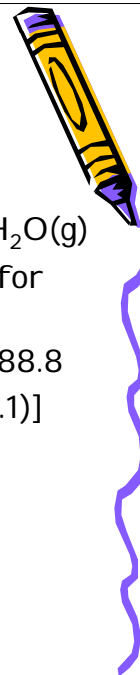
Example: combustion of ethane



Do you think entropy will increase or decrease for this reaction?

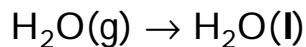
$$S^\circ(\text{J/mol}\cdot\text{K}) \quad 206.6 \quad 205.1 \quad 213.7 \quad 188.8$$

$$\begin{aligned} \Delta S_{\text{rxn}} &= [2(213.7) + 3(188.8)] - [206.6 + 3.5(205.1)] \\ &= 69.4 \text{ J/mol}\cdot\text{K} \end{aligned}$$



# Entropy

- Is it possible for the entropy of a system to decrease?



$$\begin{aligned} \Delta S_{\text{condensation}} &= 70.0 \text{ J/mol}\cdot\text{K} - 188.8 \text{ J/mol}\cdot\text{K} \\ &= -118.8 \text{ J/mol}\cdot\text{K} \end{aligned}$$

- Is this a violation of the 2<sup>nd</sup> Law because the entropy of the system is decreasing?



# Entropy

- As water vapor condenses, heat is transferred from the gas phase molecules to the surroundings

$$\begin{aligned}\Delta S_{\text{surr}} &= q_{\text{rev}}/T \\ &= q_{\text{surr}}/T \\ &= \Delta H_{\text{surr}}^{\circ}/T\end{aligned}$$

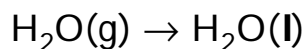
$\Delta H_{\text{surr}}^{\circ}$  is heat increase of surroundings

$$\Delta H_{\text{surr}}^{\circ} = -\Delta H_{\text{sys}}^{\circ}$$

heat gained by surroundings was lost by system



# Entropy



$$\Delta H_{\text{sys}}^{\circ} = -\Delta H_{\text{vap}}^{\circ} = -40.7 \text{ kJ/mol}$$

$$\begin{aligned}\Delta S_{\text{surr}} &= -\Delta H_{\text{sys}}^{\circ}/T \\ &= -(-40700 \text{ J/mol})/298 \text{ K} \\ &= 136.6 \text{ J/mol}\cdot\text{K}\end{aligned}$$

- The entropy of the surroundings increases by 136.6 J/mol·K



## Entropy

- If we now examine the change in entropy of the universe:

$$\begin{aligned}\Delta S_{\text{universe}} &= \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \\ &= -118.8 \text{ J/mol}\cdot\text{K} + 136.6 \text{ J/mol}\cdot\text{K} \\ &= 17.8 \text{ J/mol}\cdot\text{K}\end{aligned}$$

- The entropy of the universe increases, maintaining the validity of the 2<sup>nd</sup> Law



## Entropy

- When a substance is not in its standard state ( $P \neq 1 \text{ atm}$  or  $[A] \neq 1 \text{ M}$ ), the entropy is given by:

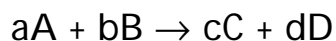
$$S = S^{\circ} - R \ln P \quad \text{or} \quad S = S^{\circ} - R \ln[A]$$

- This allows calculation under non-standard state conditions



## Entropy

- For the reaction



$$\begin{aligned}\Delta S_{\text{rxn}} &= \Delta S_{\text{rxn}}^{\circ} - R \ln \left( \frac{[C]^c [D]^d}{[A]^a [B]^b} \right) \\ &= \Delta S_{\text{rxn}}^{\circ} - R \ln [Q]\end{aligned}$$

$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad \text{reaction quotient}$$



## Free Energy

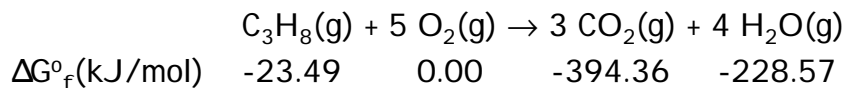
- When a change takes place in a system, some energy may be transferred in the form of heat, and some energy may be occupied by changes in entropy.
- The energy remaining may be used to perform other types of work—this is called the *free energy* of the system
- Gibbs Free Energy is defined as:

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



## Free Energy

Example: Combustion of propane



$$\begin{aligned}\Delta G^\circ_{\text{rxn}} &= [3(-394.36) + 4(-228.57)] - [(-23.49) + 5(0.00)] \\ &= -2073.87 \text{ kJ/mol}\end{aligned}$$



## Free Energy

- The same rules apply to Gibb's Free Energy as apply to enthalpy
- The  $\Delta G^\circ_{\text{rxn}}$  can be calculated from the  $\Delta G^\circ_f$  (Gibb's Free Energy of formation) of the reactants and products

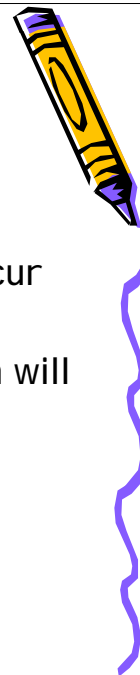
$$\Delta G^\circ_{\text{rxn}} = \sum_{\text{prods}} n_i \Delta G^\circ_f(i) - \sum_{\text{reacts}} n_i \Delta G^\circ_f(i)$$

$\Delta G^\circ_f$  of the elements in their standard form at any temperature is 0.00 kJ/mol



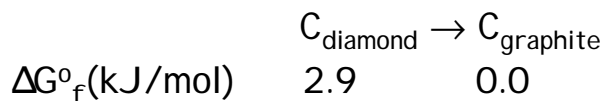
## Free Energy

- Gibb's Free Energy is a indicator of the spontaneity of a reaction:
  - If  $\Delta G$  is negative, the reaction will occur spontaneously as written
  - If  $\Delta G$  is positive, the reverse reaction will occur spontaneously
  - If  $\Delta G = 0$ , the system is in equilibrium



## Free Energy

Example: Transition of carbon from diamond form to graphite form at standard pressure



$$\Delta G^{\circ}_{\text{rxn}} = 0.0 - 2.9 = -2.9 \text{ kJ/mol}$$

Diamond spontaneously transforms to graphite at standard pressure and room temperature



## Free Energy

- Temperature can have an effect on the sign of  $\Delta G^{\circ}_{\text{rxn}}$

$$\Delta G^{\circ}_{\text{rxn}} = \Delta H^{\circ}_{\text{rxn}} - T\Delta S^{\circ}_{\text{rxn}}$$

$\Delta H^{\circ}_{\text{rxn}}$	$\Delta S^{\circ}_{\text{rxn}}$	$\Delta G^{\circ}_{\text{rxn}}$
-	+	-
+	-	+
-	-	- at low T + at high T
+	+	+ at low T - at high T



## Free Energy

$$\Delta G_{\text{rxn}} = \Delta H_{\text{rxn}} - T\Delta S_{\text{rxn}}$$

$$= \Delta H^{\circ}_{\text{rxn}} - T(\Delta S^{\circ}_{\text{rxn}} - R \ln[Q])$$

$\Delta H_{\text{rxn}} \cong \Delta H^{\circ}_{\text{rxn}}$  because pressure has very little effect on enthalpy

$$\Delta G_{\text{rxn}} = \Delta H^{\circ}_{\text{rxn}} - T\Delta S^{\circ}_{\text{rxn}} + RT \ln[Q]$$

$$\Delta H^{\circ}_{\text{rxn}} - T\Delta S^{\circ}_{\text{rxn}} = \Delta G^{\circ}_{\text{rxn}}$$

$$\Delta G_{\text{rxn}} = \Delta G^{\circ}_{\text{rxn}} + RT \ln[Q]$$



## Free Energy

- At equilibrium,  $\Delta G_{\text{rxn}} = 0$  and  $Q = K_{\text{eq}}$

$$0 = \Delta G_{\text{rxn}}^{\circ} + RT \ln K_{\text{eq}}$$

$$\Delta G_{\text{rxn}}^{\circ} = -RT \ln K_{\text{eq}}$$

relates equilibrium constant to thermodynamic functions of G, H, and S



## Free Energy

Example: Find  $K_{\text{sp}}$  for dissolution of  $\text{AgCl(s)}$

$$K_{\text{eq}} = \exp\left\{\frac{-\Delta G_{\text{rxn}}^{\circ}}{RT}\right\}$$



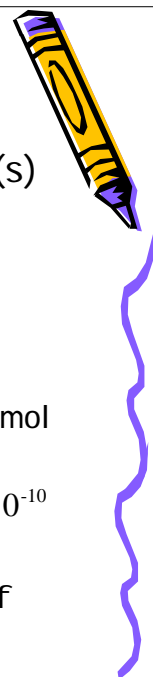
$$\Delta G_{\text{f}}^{\circ}(\text{kJ/mol}) \quad -109.79 \quad 77.11 \quad -131.23$$

$$\Delta G_{\text{rxn}}^{\circ} = [77.10 - 131.23] - [-109.79] = 55.66 \text{ kJ/mol}$$

$$K_{\text{eq}} = \exp\left\{\frac{-55660 \text{ J/mol}}{(8.314 \text{ J/mol}\cdot\text{K})(298 \text{ K})}\right\} = 1.8 \times 10^{-10}$$



Same value as reported  $K_{\text{sp}}$  in tables of solubility products





# Free Energy

- When  $\Delta G_{\text{rxn}}$  is negative, the reaction proceeds spontaneously
  - The products are thermodynamically favored
- Does this mean that the reaction actually occurs?
  - Yes! But the time frame for reaction may be remarkably slow
  - diamond  $\rightarrow$  graphite
  - methane in air  $\rightarrow$   $\text{CO}_2$  and  $\text{H}_2\text{O}$
  - The kinetics of the reaction (activation barrier, rate coefficient) may be so slow that we do not observe a chemical change

