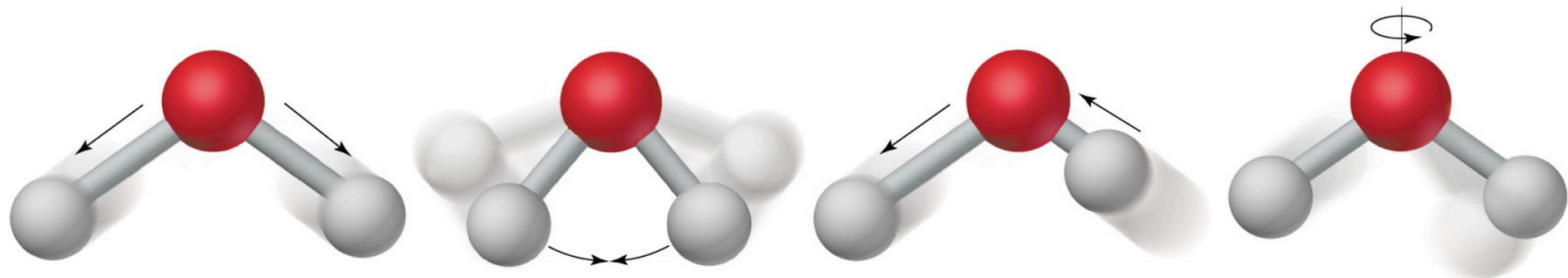


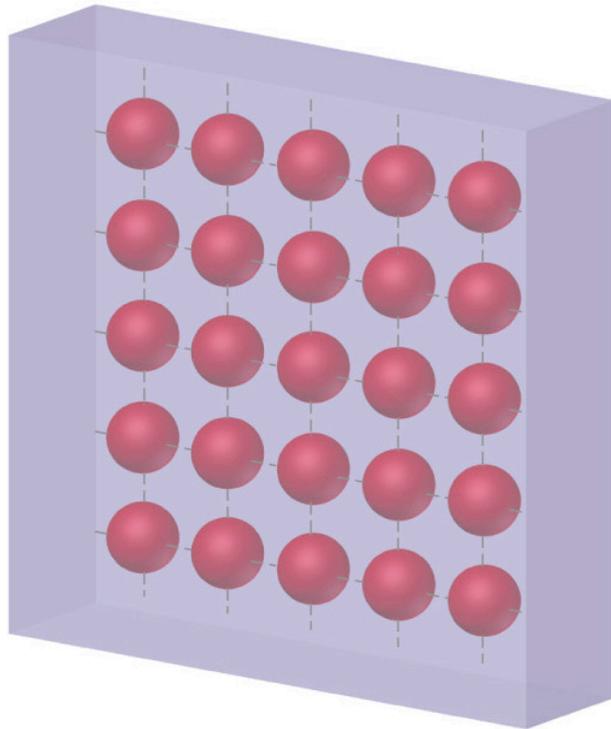
The Molecular Interpretation of Entropy

- There are three atomic modes of motion:
 - translation (the moving of a molecule from one point in space to another),
 - vibration (the shortening and lengthening of bonds, including the change in bond angles),
 - rotation (the spinning of a molecule about some axis).



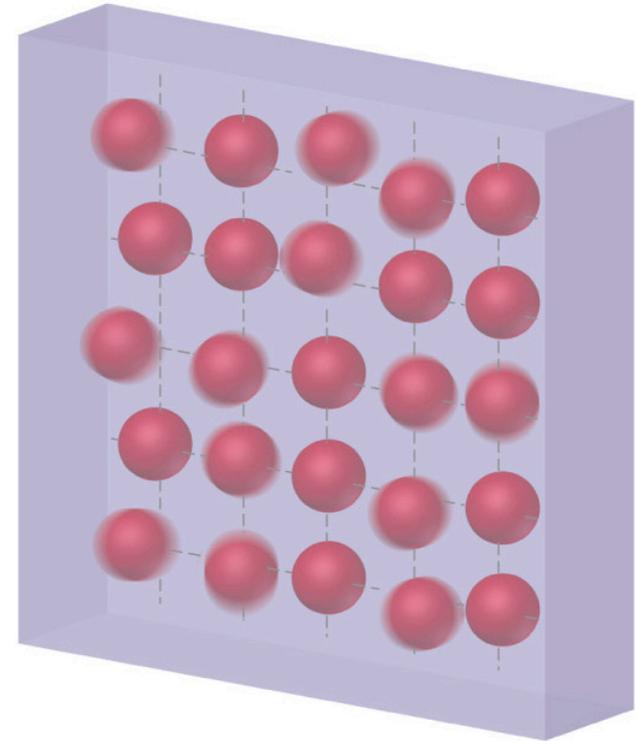
- Energy is required to get a molecule to translate, vibrate or rotate.
- The more energy stored in translation, vibration and rotation, the greater the degrees of freedom and the higher the entropy.
- In a perfect crystal at 0 K there is no translation, rotation or vibration of molecules. Therefore, this is a state of perfect order (zero entropy).

The Molecular Interpretation of Entropy



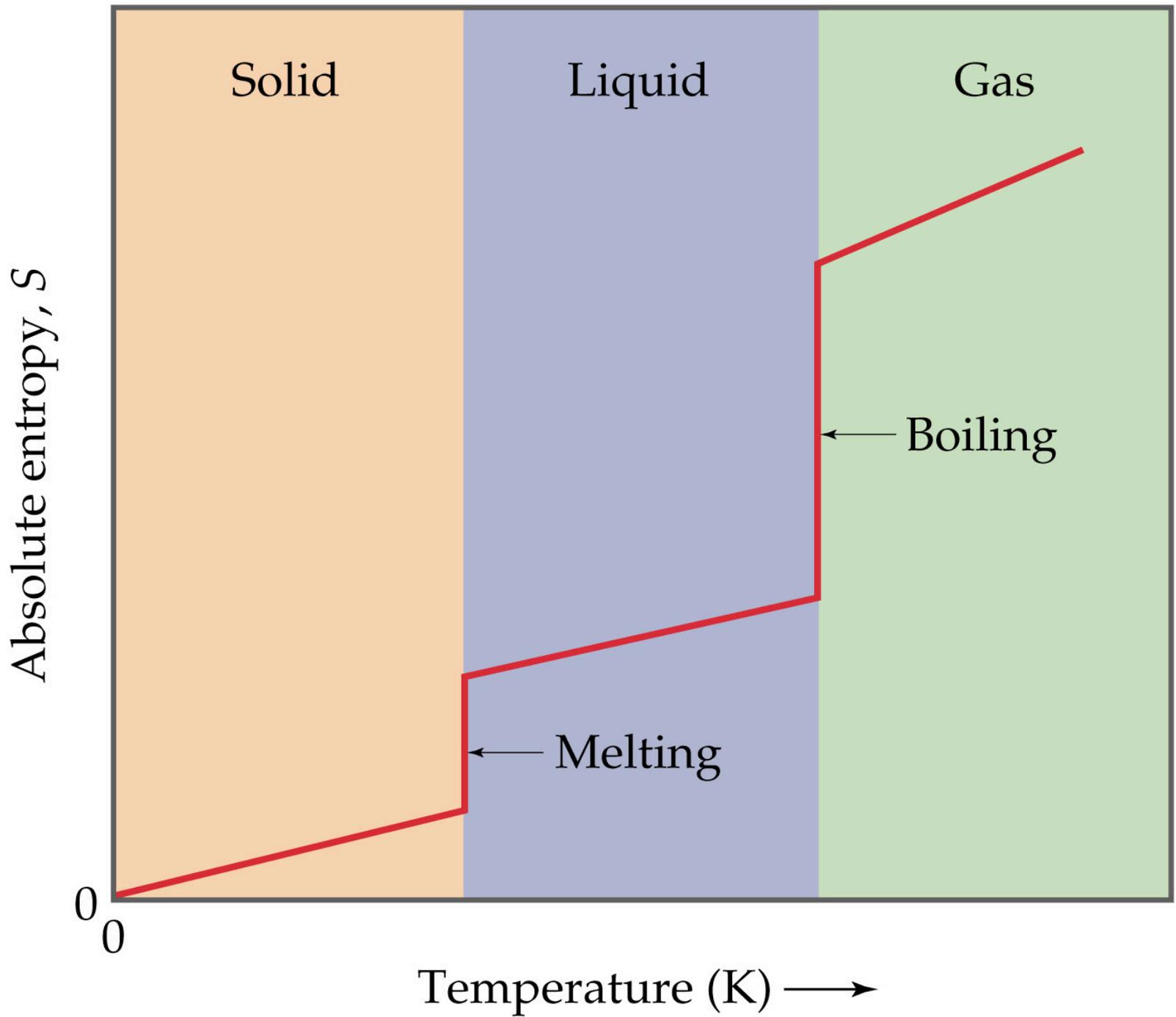
0 K
 $S = 0$

Increasing temperature
→



> 0 K
 $S > 0$

- Third Law of Thermodynamics: the entropy of a perfect crystal at 0 K is zero.
- Entropy changes dramatically at a phase change.
- As we heat a substance from absolute zero, the entropy must increase.
- If there are two different solid state forms of a substance, then the entropy increases at the solid state phase change.



- Boiling corresponds to a much greater change in entropy than melting.
- Entropy will increase when
 - liquids or solutions are formed from solids,
 - gases are formed from solids or liquids,
 - the number of gas molecules increase,
 - the temperature is increased.

Entropy Changes in Chemical Reactions

- Absolute entropy can be determined from complicated measurements.
- Standard molar entropy, S° : entropy of a substance in its standard state. Similar in concept to ΔH° .
- Units: $\text{J mol}^{-1} \text{K}^{-1}$. Note units of ΔH : kJ mol^{-1} .
- Standard molar entropies of elements are not zero.
- For a chemical reaction which produces n moles of products from m moles of reactants:

$$\Delta S^\circ = \sum nS^\circ(\text{products}) - \sum mS^\circ(\text{reactants})$$

Examples – Calculate ΔS for each of the following reactions:



Examples – Calculate ΔS for each of the following reactions:



-5.0 J K^{-1}



-198.2 J K^{-1}



189.6 J K^{-1}



-130.2 J K^{-1}

Gibbs Free Energy

- For a spontaneous reaction the entropy of the universe must increase.
- Reactions with large negative ΔH values are spontaneous.
- How do we balance ΔS and ΔH to predict whether a reaction is spontaneous?
- Gibbs free energy, G , of a state is

$$G = H - TS$$

- For a process occurring at constant temperature

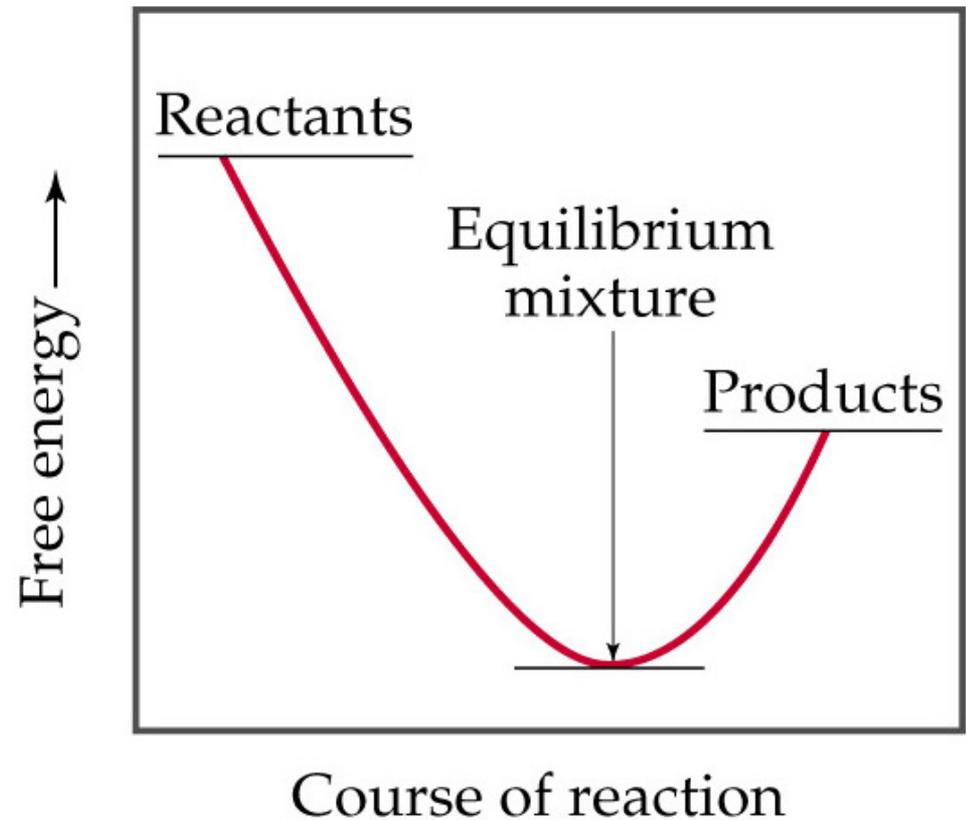
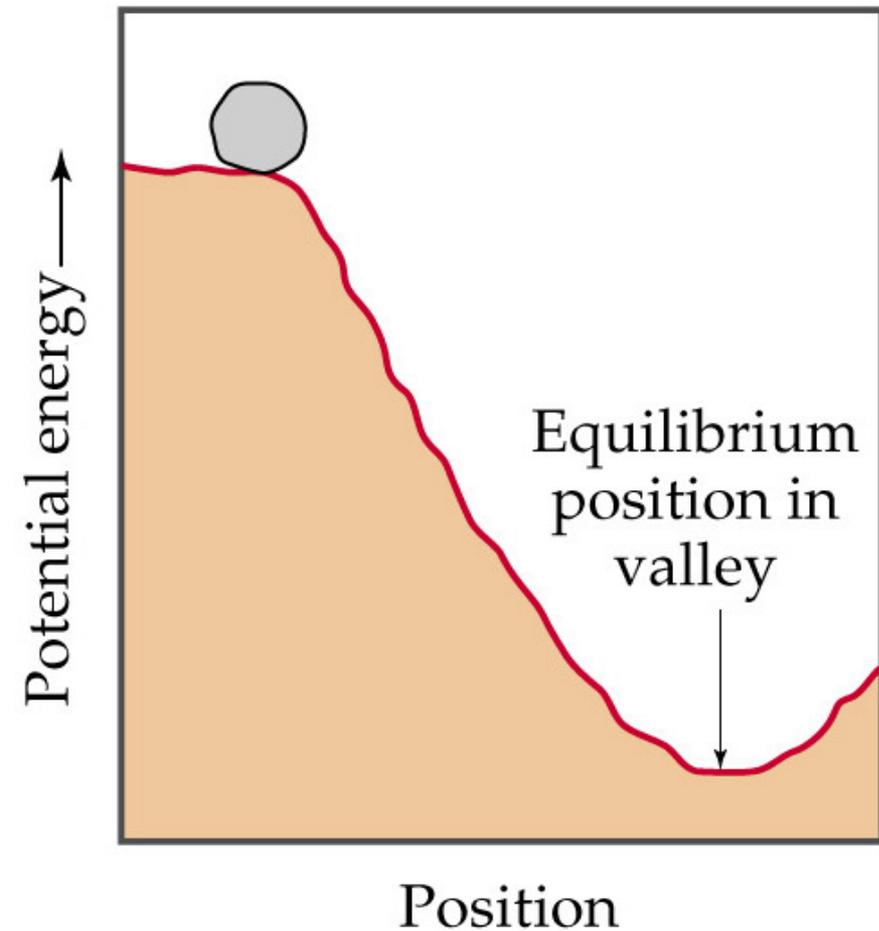


$$\Delta G = \Delta H - T\Delta S$$



- There are three important conditions:
 - If $\Delta G < 0$ then the forward reaction is spontaneous.
 - If $\Delta G = 0$ then reaction is at equilibrium and no net reaction will occur.
 - If $\Delta G > 0$ then the forward reaction is not spontaneous (reverse reaction is spontaneous). If $\Delta G > 0$, work must be supplied from the surroundings to drive the reaction.
- For a reaction the free energy of the reactants decreases to a minimum (equilibrium) and then increases to the free energy of the products.

Gibbs Free Energy



Gibbs Free Energy

- Consider the formation of ammonia from nitrogen and hydrogen:



- Initially ammonia will be produced spontaneously ($Q < K_{eq}$).
- After some time, the ammonia will spontaneously react to form N_2 and H_2 ($Q > K_{eq}$).
- At equilibrium, $\Delta G = 0$ and $Q = K_{eq}$.

Standard Free-Energy Changes

- We can tabulate standard free-energies of formation, ΔG_f° (c.f. standard enthalpies of formation).
- Standard states are: pure solid, pure liquid, 1 atm (gas), 1 M concentration (solution), and $\Delta G_f^\circ = 0$ for elements.
- ΔG° for a process is given by
$$\Delta G^\circ = \sum n \Delta G_f^\circ (\text{products}) - \sum m \Delta G_f^\circ (\text{reactants})$$
- The quantity ΔG° for a reaction tells us whether a mixture of substances will spontaneously react to produce more reactants ($\Delta G^\circ > 0$) or products ($\Delta G^\circ < 0$).

Examples – Calculate ΔH , ΔS , and ΔG (by both methods) for each of the following reactions:



1. $\Delta H = -802.3 \text{ kJ}$, $\Delta S = -5.0 \text{ J K}^{-1}$
 $\Delta G = -800.8 \text{ kJ}$ or -800.7 kJ
2. $\Delta H = -92.38 \text{ kJ}$, $\Delta S = -198.24 \text{ J K}^{-1}$
 $\Delta G = -33.3 \text{ kJ}$ or -33.3 kJ
3. $\Delta H = 196.6 \text{ kJ}$, $\Delta S = 189.6 \text{ J K}^{-1}$
 $\Delta G = 140.1 \text{ kJ}$ or 140.0 kJ
4. $\Delta H = -74.9 \text{ kJ}$, $\Delta S = -130.19 \text{ J K}^{-1}$
 $\Delta G = -36.1 \text{ kJ}$ or -35.9 kJ

Free Energy and Temperature

- Focus on $\Delta G = \Delta H - T\Delta S$:
 - If $\Delta H < 0$ and $\Delta S > 0$, then ΔG is always negative.
 - If $\Delta H > 0$ and $\Delta S < 0$, then ΔG is always positive. (That is, the reverse of 1.)
 - If $\Delta H < 0$ and $\Delta S < 0$, then ΔG is negative at low temperatures.
 - If $\Delta H > 0$ and $\Delta S > 0$, then ΔG is negative at high temperatures.
- Even though a reaction has a negative ΔG it may occur too slowly to be observed.

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

ΔH	ΔS	ΔG
-	+	Always -
+	-	Always +
+	+	- at high T + at low T
-	-	+ at high T - at low T