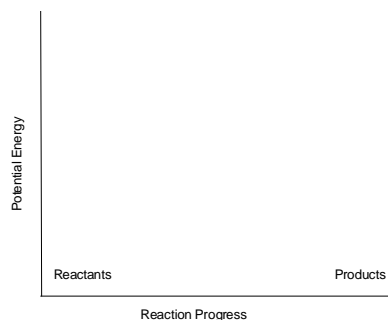## Spontaneity, Entropy and Free Energy

Spontaneous ≠ Fast

Thermodynamics vs Kinetics

Primary goal of thermodynamics**:** Predict the *tendency* for a reaction to occur.

– Compare reactants and products

1

Entropy

So far we have discussed the use of Enthalpy (ΔH) for learning something about the tendency of a reaction to release or require energy as heat **if** it were to proceed as written.

ΔH isn't the whole story. We also need to consider another factor, **Entropy (S)**. The combination of Enthalpy and Entropy will help us deal with the **if**.

Entropy, "disorder", and probability:

$$S = k_B \ln W$$
$$k_B = R/N_A$$

For complex systems, determining S is a challenge.
- Focus on entropy *changes*, $\Delta S = q_{rev}/T$
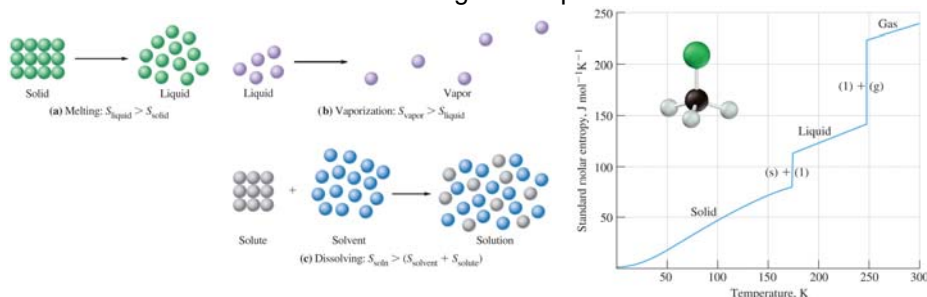
2

1

Entropy

Entropy is a critical component of the Laws of Thermodynamics:

- **1st Law:** Total energy of the universe is constant.

- **2nd Law:** The total <u>entropy</u> of the universe is always increasing.
  - So, spontaneous processes lead to increased $\Delta S_{universe}$

- **3rd Law:** The <u>entropy</u> of a pure, perfectly formed crystalline substance at absolute zero is zero.
  - So, since the minimum value for S is zero, S for any material is always positive!

3

Important Entropy Considerations

1. S is temperature dependent.
2. For similar materials, S(gases) >> S(liquids) > S(solids)
   - $\Delta S_{phase\ change} = \Delta H_{phase\ change}/T$
3. S for more complex materials is larger than for simpler molecules.
4. S for ionic materials becomes larger as inter-ionic attractions get smaller
5. S increases when a pure liquid (solid) dissolves in a solvent.
6. S increases when a dissolved gas escapes from a solution

(a) Melting: $S_{liquid} > S_{solid}$ (b) Vaporization: $S_{vapor} > S_{liquid}$
(c) Dissolving: $S_{soln} > (S_{solvent} + S_{solute})$

Entropy and Spontaneity

Because of the 2nd Law, $\Delta S_{universe}$ must be positive for a product-favored reaction.

- $\Delta S_{universe}$ is a combination of the entropy change of the reaction (ΔS_{system}) and the effect on the rest of the universe ($\Delta S_{surroundings}$). Mathematically:

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

- How do we determine the two components?

$$\Delta S_{system} = \Sigma S_{products} - \Sigma S_{reactants}$$

$$\Delta S_{surroundings} = \frac{\text{Heat energy absorbed}}{T} = \frac{-\Delta H_{system}}{T}$$

$$\Delta S_{universe} = \Delta S_{system} + \frac{(-\Delta H_{system})}{T}$$

5

Entropy and Spontaneity

- What do these laws (and what we observe) say about entropy and spontaneity?

$$\Delta S_{universe} = \Delta S_{system} + \frac{(-\Delta H_{system})}{T}$$

- The **_Combination_** of enthalpy and entropy determines spontaneity of a reaction.

Process	Sign of ΔS_{system}	Sign of ΔH_{system}
Product-favored		
Reactant-favored		

6

3

Entropy and Free Energy

This result of this combination of effects is the **Gibbs Free Energy Change** (ΔG):

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

$$\Delta S_{universe} = \frac{-\Delta H_{system}}{T} + \Delta S_{system}$$

7

Free Energy and Spontaneity

FOR A SPONTANEOUS PROCESS, ΔG MUST BE NEGATIVE!

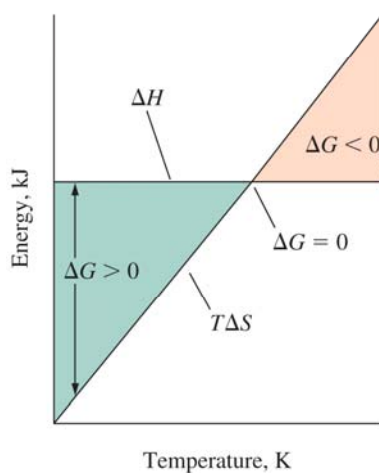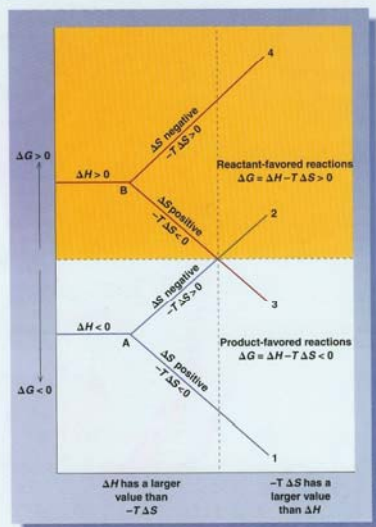Because of temperature dependence of ΔG, we can (sometimes) push a reaction in either direction! (Figure 19-9)

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

Sign of ΔH	Sign of ΔS	Sign of ΔG	Spontaneous?
-	+		
+	-		
-	-		
+	+		

8

4

Free Energy and Spontaneity

Kotz: Chemistry & Chemical Reactivity, 4/e
Figure 20.8

Copyright © 2007 Pearson Prentice Hall, Inc.

9

Predicting Spontaneity

As with ΔH^o and ΔS^o, ΔG^o for a reaction can be predicted using the appropriate energies of formation

$$\Delta G^o_{rxn} = \Sigma[n\Delta G^o_f(products)] - \Sigma[n\Delta G^o_f(reactants)]$$

This fact, property, along with $\Delta G = \Delta H - T\Delta S$, lets us make several predictions about the tendency for a reaction.

Example: Is the reduction of magnesia, MgO, with carbon a product-favored process at 25°C? If not, what temperature does it become so?

$$MgO(s) + C(graphite) \rightarrow Mg(s) + CO(g)$$

10

5

What about nonstandard conditions?

ΔG will change as temperature and composition of system varies!
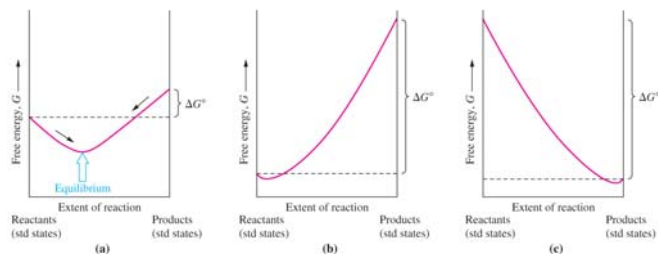
$$\Delta G = \Delta G^o + RT\ln Q$$

Q = reaction quotient

R = gas constant in "energy units" = 8.3145 J/mol K

Conceptually: ΔG = "$G_{products} - G_{reactants}$"

Equilibrium: Special situation when $G_{products} = G_{reactants}$

$$\Delta G = 0 = \Delta G^o + RT\ln K$$

Free Energy and Spontaneity
A Final Look

- **Generalizations:**

$\Delta G^o < 0$	Forward reaction is spontaneous at standard state. ("product-favored")
$\Delta G^o > 0$	Forward reaction is non spontaneous at standard state. ("reactant-favored")
$\Delta G^o = 0$	Reaction is at equilibrium at standard state
$\Delta G < 0$	Forward reaction is spontaneous under the conditions given. ("product-favored")
$\Delta G > 0$	Forward reaction is non-spontaneous under the conditions given. ("reactant-favored")

TABLE 19.1   Criteria for Spontaneous Change: $\Delta G = \Delta H - T\Delta S$

Case	ΔH	ΔS	ΔG	Result	Example
1.	−	+	−	spontaneous at all temp.	$2\,N_2O(g) \longrightarrow 2\,N_2(g) + O_2(g)$
2.	−	−	− / +	spontaneous at low temp. / nonspontaneous at high temp.	$H_2O(l) \longrightarrow H_2O(s)$
3.	+	+	+ / −	nonspontaneous at low temp. / spontaneous at high temp.	$NH_3(g) \longrightarrow N_2(g) + 3\,H_2(g)$
4.	+	−	+	nonspontaneous at all temp.	$3\,O_2(g) \longrightarrow 2\,O_3(g)$