Module 8: Thermodynamics II, Lecture 4

Gibbs Free Energy and Spontaneous Process

Learning Objective	Openstax 2e Chapter
Gibbs Free Energy	**16.4**

Suggested Practice Problems

Chapter 16 Exercises – Questions: 31, 33 (use Appendix G), 35, 37 (use Appendix G)

Answers can be found in the Chapter 16 Answer Key
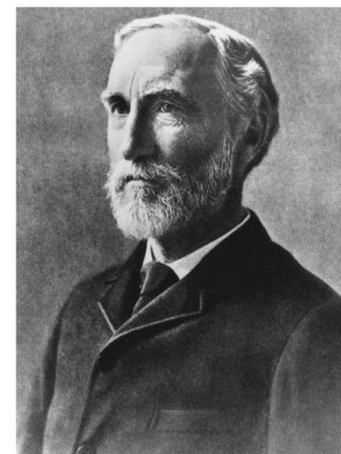
Criterion for a Spontaneous Change

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

The 2nd law says, for a spontaneous change:

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} > 0$$

If the temperature and pressure of the surroundings are constant:

$$\Delta S_{univ} = \Delta S_{sys} + [-\Delta H_{sys} / T] = \frac{T\Delta S_{sys} - \Delta H_{sys}}{T}$$

$$= \frac{-(\Delta H_{sys} - T\Delta S_{sys})}{T} = \frac{-\Delta(H_{sys} - TS_{sys})}{T}$$

Copyright © 2007 Pearson Prentice Hall, Inc.

J. Willard Gibbs
1839-1903

We can define a new <u>state function</u>: G = H - TS   (known as the Gibbs Free Energy)

Thus, $\Delta S_{univ} = \dfrac{-\Delta G_{sys}}{T} > 0$

The 2nd law becomes $\Delta G_{sys} < 0$ for any spontaneous process.

Gibbs Free Energy

$$G = H - TS$$

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

For any process to be spontaneous, $\Delta G < 0$

Which can be a result of fine interplay between ΔH and ΔS

Criterion for a Spontaneous Change

$\Delta S_{univ} > 0$	$\Delta G_{sys} < 0$	spontaneous
$\Delta S_{univ} < 0$	$\Delta G_{sys} > 0$	nonspontaneous
$\Delta S_{univ} = 0$	$\Delta G_{sys} = 0$	at equilibrium

What's "Free" about ΔG?

ΔH = Energy produced by the process

$T\Delta S$ = Energy lost to the surrounding

ΔG = Energy available (or "free") to do useful work by the process

Free Energy Change in Spontaneous Process

Squeeze

$$NH_4NO_3(s) \longrightarrow NH_4^+(aq) + NO_3^-(aq)$$

$\Delta H°$ is the standard enthalpy change at P = 1 bar, T = 25 °C or 298.15 K

Liquid and gasses must be PURE

!

Solutions be at 1 M concentration

$\Delta H° = + 27$ kJ mol^{-1} Endothermic reaction required for the 'cooling effect'

$\Delta S° = + 109$ J K^{-1} mol^{-1} (see lecture slide in L3)

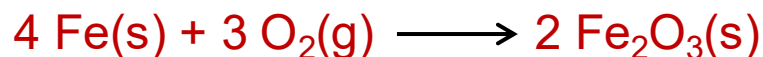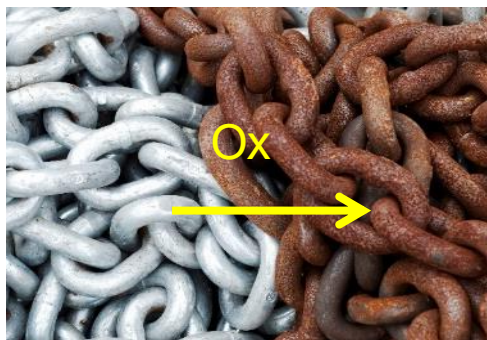$$\Delta G° = \Delta H° - T\Delta S°$$

At 298.15 K $\Delta G° = 27 \times 10^3$ J mol^{-1} – (298.15 K $\times$ 109 J mol^{-1} K^{-1})= –5,500 J mol^{-1}

Positive

Larger Positive

This process is spontaneous despite a positive $\Delta H°$, due to the largely negative –T$\Delta S°$

This spontaneity is '**ENTROPY** driven'.

4

Free Energy Change in Spontaneous Process

$$4\ Fe(s) + 3\ O_2(g) \longrightarrow 2\ Fe_2O_3(s)$$

$\Delta H° = -1648\ kJ\ mol^{-1}$ Rusting is an exothermic process

$\Delta S° = -549\ J\ K^{-1}\ mol^{-1}$

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

At 298.15 K $\Delta G° = -1.6 \times 10^6\ J\ mol^{-1} - \{298.15\ K \times (-549)\ J\ mol^{-1}\ K^{-1}\} = -1480\ kJ\ mol^{-1}$

Large Negative

Small Negative

This process is spontaneous due to a largely negative $\Delta H°$,
that cannot be compensated even by a negative $\Delta S°$

This spontaneity is 'ENTHALPY driven'.

5

Free Energy Change in Spontaneous Process

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

	ΔH is positive	ΔH is negative
ΔS is positive	at low T, ΔG is positive (**NOT spontaneous**) at high T, ΔG is negative (**spontaneous**)	ΔG is negative (**spontaneous**)
ΔS is negative	ΔG is positive (**NOT spontaneous**)	at low T, ΔG is negative (**spontaneous**) at high T, ΔG is positive (**NOT spontaneous**)

Free Energy Change in Spontaneous Process

Does the following reaction occur spontaneously or not at 298 K and other temperatures?

$$2 \text{ N}_2\text{O (g)} \rightarrow 2 \text{ N}_2 \text{ (g)} + \text{O}_2 \text{ (g)}$$

	$\Delta_f H^0$ (kJ mol^{-1})	S^0 $(J\ mol^{-1}\ K^{-1})$
N$_2$O (g)	81.6	220.0
N$_2$ (g)	0	191.6
O$_2$ (g)	0	205.2

$$\Delta_r H^0 = 2\left(0\,\frac{kJ}{mol}\right) + 0\,\frac{kJ}{mol} - 2\left(81.6\,\frac{kJ}{mol}\right) = -163.2\,\frac{kJ}{mol}$$

$$\Delta_r S^0 = 2\left(191.6\,\frac{J}{mol\cdot K}\right) + \left(205.2\,\frac{J}{mol\cdot K}\right) - 2\left(220.0\,\frac{J}{mol\cdot K}\right) = 148.4\,\frac{J}{mol\cdot K}$$

$\Delta_r H^\circ < 0$

$\Delta_r S^\circ > 0$

$\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ < 0$, spontaneous at all temperatures!

Free Energy Change in Reversible Process

**Δ_rH for freezing of water is -6.01 kJ·mol^{-1} at atmospheric pressure.\
What is the entropy change for freezing of water at 0 °C?**

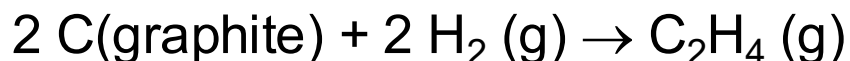$$H_2O \text{ (l)} \rightarrow H_2O \text{ (s)}$$

at freezing point of water, freezing $\rightleftarrows$ melting is reversible (i.e., ice and liquid water are at equilibrium), thus $\Delta G = \Delta H - T\Delta S = 0$

$$\Delta S = \frac{\Delta H_{fus}}{T} = \frac{-6010\,J \cdot mol^{-1}}{273.15\,K} = -22.0\,J \cdot mol^{-1} \cdot K^{-1}$$

Spontaneous Process

Does the following reaction occur spontaneously or not at 298 K and other temperatures?

$2\ C(graphite) + 2\ H_2\ (g) \rightarrow C_2H_4\ (g)$

$\Delta_rH° = 52.26\ kJ·mol^{-1}$ $\hspace{2cm}$ $S°_{H2(g)} = 130\ J·mol^{-1}·K^{-1}$,

$S°_{graphite} = 5.74\ J·mol^{-1}·K^{-1}$ $\hspace{2cm}$ $S°_{C2H4(g)} = 229.6\ J·mol^{-1}·K^{-1}$

Let us calculate entropy change:
$\Delta S° = 229.6 - (2\ x\ 5.74 + 2\ x\ 130)\ J·mol^{-1}·K^{-1} = -41.9\ J·mol^{-1}·K^{-1}$

Because $\Delta H° > 0$, and $- T\Delta S° > 0$,

$$\Delta G° = \Delta H° - T\Delta S° > 0.$$

Thus, the process is non-spontaneous at all temperatures!

Methods to Calculate $\Delta_r G°$

What's the $\Delta_r G°$ of limestone converting into quicklime?

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

Method 1

Find out $\Delta_r H°$ and $\Delta_r S°$ from Data Tables, and then calculate $\Delta_r G°$

$\Delta_r H° = \sum a_j \cdot \Delta_f H°(\text{products}) - \sum a_i \cdot \Delta_f H°(\text{reactants})$

$\quad = \Delta_f H°(CaO\,(s)) + \Delta_f H°(CO_2\,(g)) - \Delta_f H°(CaCO_3\,(s))$

$\quad = -635.1 \text{ kJ mol}^{-1} + (-393.5 \text{ kJ mol}^{-1}) - (-1207 \text{ kJ mol}^{-1})$

$\quad = 178.4 \text{ kJ mol}^{-1}$

$\Delta_r S° = \sum a_j \cdot S°(\text{products}) - \sum a_i \cdot S°(\text{reactants})$

$\quad = S°(CaO\,(s)) + S°(CO_2\,(g)) - S°(CaCO_3\,(s))$

$\quad = 39.75 \text{ J mol}^{-1}\,K^{-1} + 213.7 \text{ J mol}^{-1}\,K^{-1} - 92.9 \text{ J mol}^{-1}\,K^{-1}$

$\quad = 160. \text{ J mol}^{-1}\,K^{-1}$

$\Delta_r G° = \Delta_r H° - T\Delta_r S° = 131 \times 10^3 \text{ J mol}^{-1}$ **(at T = 298.15 K)**

Methods to Calculate $\Delta_r G°$

What's the $\Delta_r G°$ of limestone converting into quicklime?

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

Method 2

Calculate $\Delta_r G°$ directly from $\Delta_f G°$ values given in the Data Tables.

$\Delta_r G° = \sum a_j \cdot \Delta_f \boldsymbol{G°}(products) - \sum a_i \cdot \Delta_f \boldsymbol{G°}(reactants)$

   $= \Delta_f \boldsymbol{G°}(CaO\,(s)) + \Delta_f \boldsymbol{G°}(CO_2\,(g)) - \Delta_f \boldsymbol{G°}(CaCO_3\,(s))$

   $= -604.0 \text{ kJ mol}^{-1} + (-394.4 \text{ kJ mol}^{-1}) - (-1129 \text{ kJ mol}^{-1})$

   $= 130.6 \text{ kJ mol}^{-1}$

Note: Method 2 is restricted to T = 298.15 K only
(because all $\Delta_f G°$ values provided are calculated at T = 298.15 K)

Free Energy Changes for Coupled Reactions

As with enthalpy (H), free energy changes for reactions are additive

Reaction #3 = Reaction #1 + Reaction #2
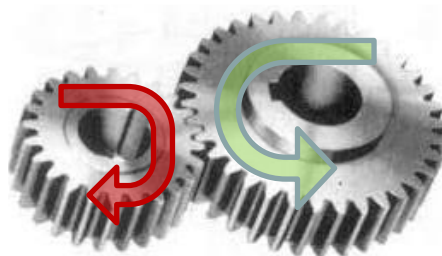
Then, $\Delta G_3 = \Delta G_1 + \Delta G_2$

How to drive a non-spontaneous reaction?

❑ Change temperature or pressure

❑ Use the "additive" nature of free energy and couple it with a spontaneous reaction

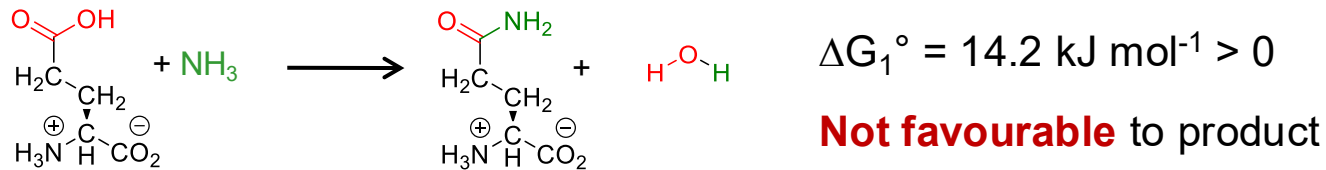If reaction #1 is non-spontaneous (ΔG_1 is positive)

If reaction #2 is spontaneous (ΔG_2 is larger negative)

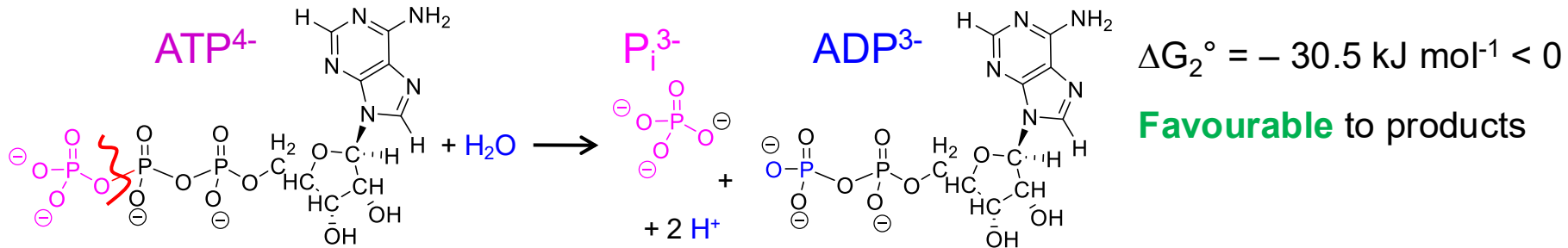Then coupling them together will make reaction #3 spontaneous (ΔG_3 negative)

Examples of Coupled Reactions

Reaction #1: Amide bond formation **Glutamic acid** to Glutamine

$\Delta G_1° = 14.2 \text{ kJ mol}^{-1} > 0$
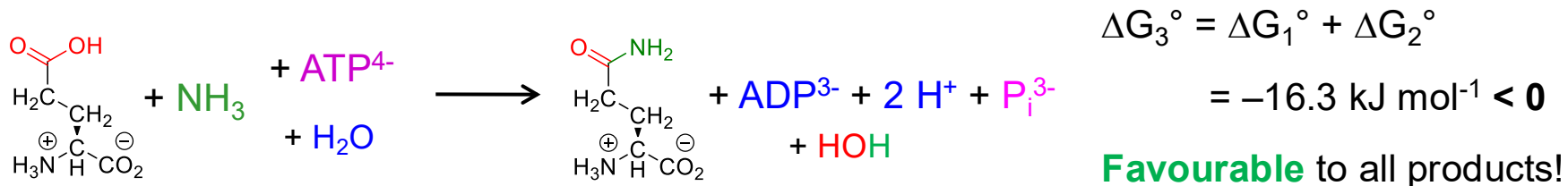
Not favourable to product

In order to **force** an unfavourable reaction to happen, pair it up with a far more energetically favourable conversion.

Reaction #2: ATP hydrolysis
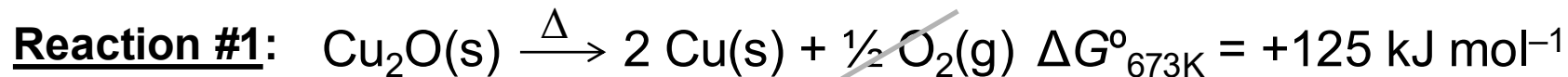

$\Delta G_2° = -30.5 \text{ kJ mol}^{-1} < 0$

Favourable to products

Reaction #3 = Reaction #1 + Reaction #2

$\Delta G_3° = \Delta G_1° + \Delta G_2°$

$= -16.3 \text{ kJ mol}^{-1} \textbf{< 0}$

Favourable to all products!

Examples of Coupled Reactions

Smelting Copper Ore

Reaction #1: $Cu_2O(s) \xrightarrow{\Delta} 2\ Cu(s) + \frac{1}{2}\ O_2(g)$ $\Delta G^o_{673K} = +125$ kJ mol^{-1}

This reaction is **non-spontaneous** even at 673 K

Reaction #2: $C(s) + \frac{1}{2}\ O_2(g) \longrightarrow CO(g)$ $\Delta G^o_{673K} = -175$ kJ mol^{-1}

$Cu_2O(s) + C(s) \longrightarrow 2\ Cu(s) + CO(g)$ $\Delta G^o_{673K} = -50$ kJ mol^{-1}

Combined reaction of Reaction #1 and Reaction #2 is **spontaneous** at 673 K.