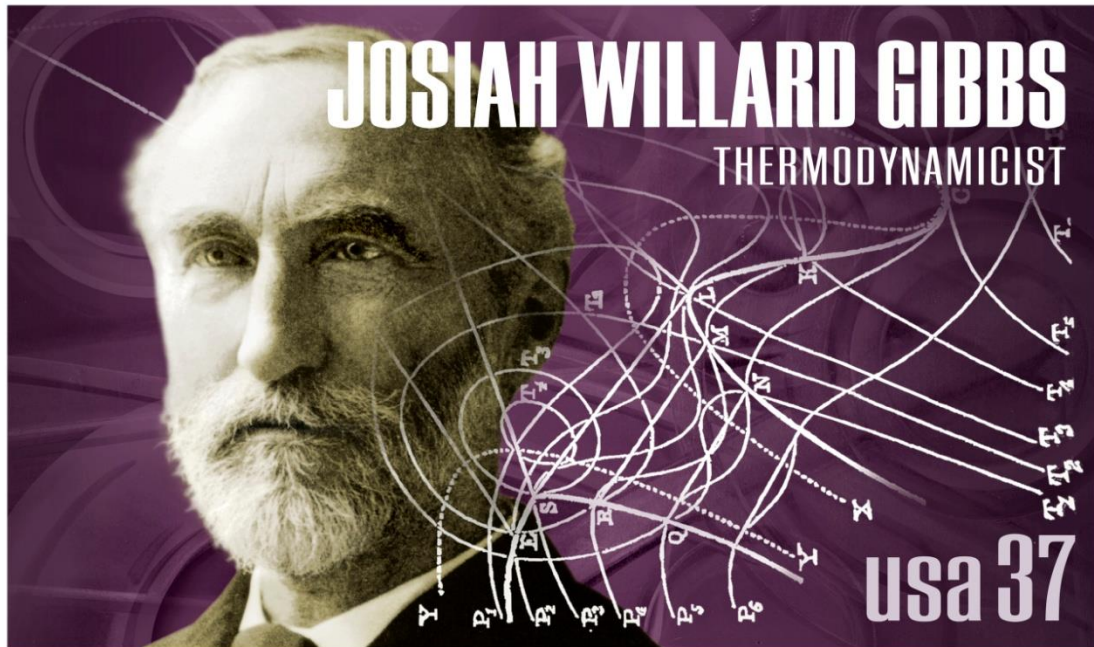


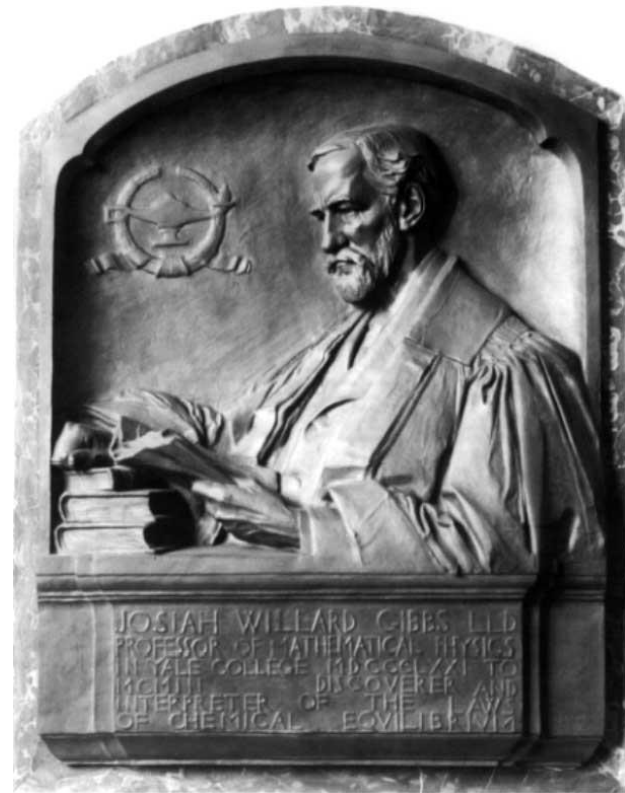
# Free Energy (G)

## Deciding If a Reaction Can Happen

**Josiah Willard Gibbs** (February 11, 1839 – April 28, 1903) was an American theoretical physicist, chemist, and mathematician. He devised much of the theoretical foundation for chemical thermodynamics as well as physical chemistry. Yale University awarded Gibbs the first American Ph.D. in engineering in 1863, and he spent his entire career at Yale.



2005



# Gibbs Free Energy

For a constant-temperature process:

**Gibbs free energy (G)**

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

Gibbs-Helmholtz Equation

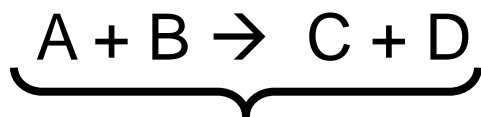
$\Delta G < 0$  The reaction is spontaneous in the forward direction.

**Spontaneous = Thermodynamically Favored**

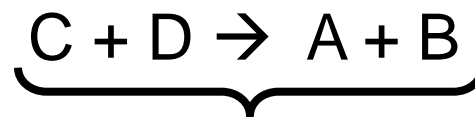
(Reaction CAN happen as written)

$\Delta G > 0$  The reaction is nonspontaneous as written. The reaction is spontaneous in the reverse direction.

$\Delta G = 0$  The reaction is at equilibrium.



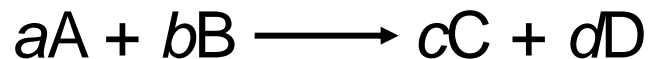
$\Delta G_{\text{forward}}$



$\Delta G_{\text{reverse}}$

$$\Delta G_{\text{forward}} = - \Delta G_{\text{reverse}}$$

The **standard free-energy of reaction** ( $\Delta G_{\text{rxn}}^0$ ) is the free-energy change for a reaction when it occurs under standard-state conditions.



$$\Delta G_{\text{rxn}}^0 = [c\Delta G_{\text{f}}^0(\text{C}) + d\Delta G_{\text{f}}^0(\text{D})] - [a\Delta G_{\text{f}}^0(\text{A}) + b\Delta G_{\text{f}}^0(\text{B})]$$

$$\Delta G_{\text{rxn}}^0 = \sum n\Delta G_{\text{f}}^0(\text{products}) - \sum m\Delta G_{\text{f}}^0(\text{reactants})$$

**Standard free energy of formation** ( $\Delta G_{\text{f}}^0$ ) is the free-energy change that occurs when **1 mole** of the compound is formed from its elements in their standard states.

$\Delta G_{\text{f}}^0$  of any element in its stable form is zero.

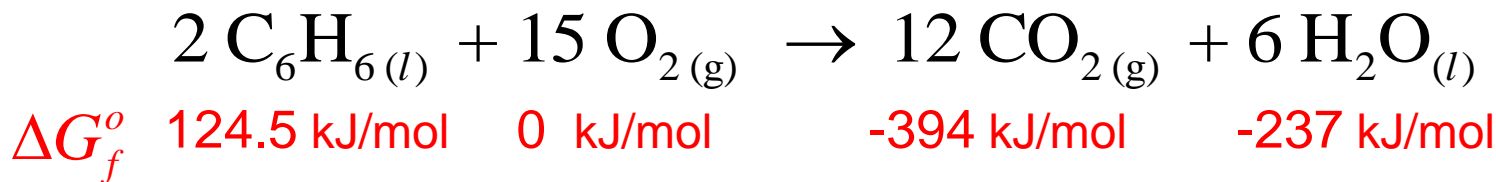
#### Conventions for Standard States

State of Matter	Standard State
Gas	1 atm pressure
Liquid	Pure liquid
Solid	Pure solid
Elements*	$\Delta G_{\text{f}}^0 = 0$
Solution	1 molar concentration

\*The most stable allotropic form at 25°C and 1 atm.

# Example Problem 1

What is the standard free-energy change for the following reaction at 25 °C?



$$\Delta G_{rxn}^\circ = \sum n \Delta G_f^\circ (\text{products}) - \sum n \Delta G_f^\circ (\text{reactants})$$

$$\Delta G_{rxn}^\circ = \left[ (12) \left( -394 \frac{\text{kJ}}{\text{mol}} \right) + (6) \left( -237 \frac{\text{kJ}}{\text{mol}} \right) \right] - \left[ (2) \left( 124.5 \frac{\text{kJ}}{\text{mol}} \right) \right]$$

$$\Delta G_{rxn}^\circ = -6405 \frac{\text{kJ}}{\text{mol}}$$

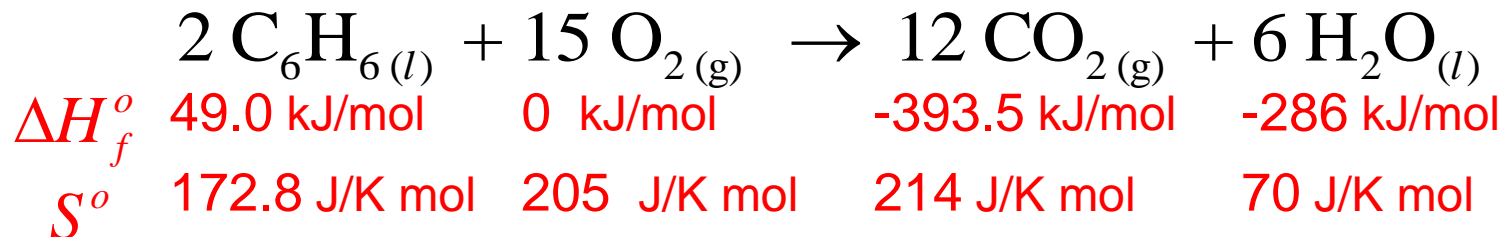
Is the reaction spontaneous at 25 °C?

$$\Delta G^\circ = -6405 \text{ kJ} < 0$$

spontaneous

## Example Problem 2

What is the standard free-energy change for the following reaction at 25 °C? Using enthalpy & entropy changes for the reaction.



$$\Delta H_{rxn}^\circ = \sum n \Delta H_f^\circ (\text{products}) - \sum n \Delta H_f^\circ (\text{reactants})$$

$$\Delta H_{rxn}^\circ = \left[ (12) \left( -393.5 \frac{\text{kJ}}{\text{mol}} \right) + (6) \left( -286 \frac{\text{kJ}}{\text{mol}} \right) \right] - \left[ (2) \left( 49.0 \frac{\text{kJ}}{\text{mol}} \right) \right]$$

$$\Delta H_{rxn}^\circ = -6536 \frac{\text{kJ}}{\text{mol}} \quad \text{Very Exothermic}$$

$$\Delta S_{rxn}^\circ = \sum n S^\circ (\text{products}) - \sum n S^\circ (\text{reactants})$$

$$\Delta S_{rxn}^\circ = \left[ (12) \left( 214 \frac{\text{J}}{\text{K}\cdot\text{mol}} \right) + (6) \left( 70 \frac{\text{J}}{\text{K}\cdot\text{mol}} \right) \right] - \left[ (2) \left( 172.8 \frac{\text{J}}{\text{K}\cdot\text{mol}} \right) + (15) \left( 205 \frac{\text{J}}{\text{K}\cdot\text{mol}} \right) \right]$$

$$\Delta S_{rxn}^\circ = -433 \frac{\text{J}}{\text{K}\cdot\text{mol}} \quad \text{Large DECREASE in entropy}$$

$$\Delta G_{rxn}^\circ = \Delta H_{rxn}^\circ - T \Delta S_{rxn}^\circ = -6536 \frac{\text{kJ}}{\text{mol}} - (298\text{K}) \left( -0.433 \frac{\text{kJ}}{\text{K}\cdot\text{mol}} \right) = -6407 \frac{\text{kJ}}{\text{mol}}$$

Comparing  $\Delta G^\circ$ : -6405 kJ/mol to -6407 kJ/mol (close but usually not exactly the same)

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

Each “driving force” can say either “yes” or “no” to the reaction.  
What happens if they disagree?

$\Delta H$	$\Delta S$	$\Delta G$	Example
(-) “Yes” Exothermic	(+) “Yes” S increase	(-) “Yes” Reaction always proceeds spontaneously at all temperatures	$2H_2O_{2(aq)} \rightarrow 2H_2O_{(l)} + O_{2(g)}$
(-) “Yes” Exothermic	(-) “No” S decreases	(-) “Yes, but.....” Reaction spontaneous only <u>below a certain temperature</u>	$NH_{3(g)} + HCl_{(g)} \rightarrow NH_4Cl_{(s)}$
(+) “No” Endothermic	(+) “Yes” S increase	(-) “Yes, but.....” Reaction spontaneous only <u>above a certain temperature</u>	$2HgO_{(s)} \rightarrow 2Hg_{(l)} + O_{2(g)}$
(+) “No” Endothermic	(-) “No” S decreases	(+) “No” Reaction <u>Only</u> proceeds in the <u>REVERSE</u> direction at all temperatures	$3O_{2(g)} \rightarrow 2O_{3(g)}$

# Temperature and Spontaneity of Chemical Reactions



$$\Delta H^0 = 177.8 \text{ kJ} \quad (\text{No})$$

$$\Delta S^0 = 160.5 \text{ J/K} \quad (\text{Yes})$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

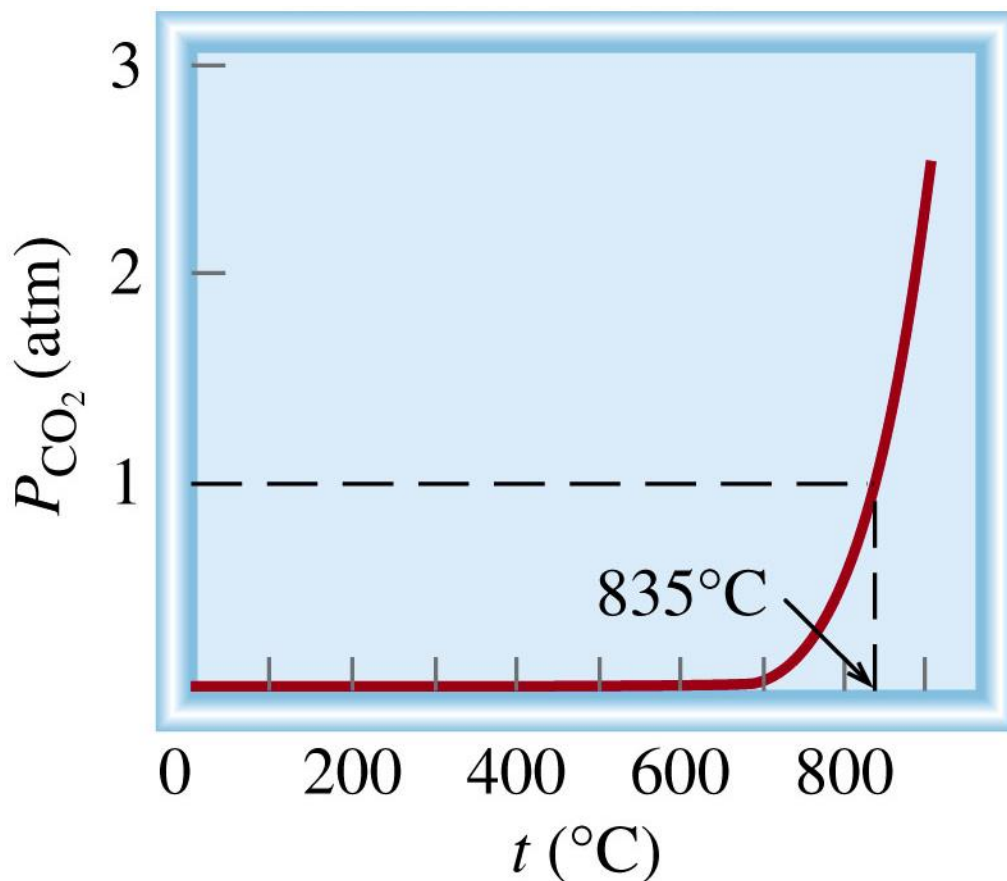
$$\text{At } 25 \text{ }^\circ\text{C}, \Delta G^0 = 130.0 \text{ kJ}$$

Nonspontaneous at 25°C

But, could happen at a higher temp.

$$\Delta G^0 = 0 \text{ at } 835 \text{ }^\circ\text{C}$$

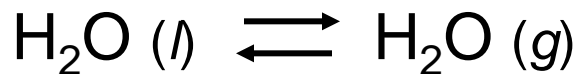
## Equilibrium Pressure of CO<sub>2</sub>





# Gibbs Free Energy and Phase Transitions

$$\Delta G^0 = 0 = \Delta H^0 - T\Delta S^0$$



$$\Delta S = \frac{\Delta H}{T} = \frac{40.79 \text{ kJ}}{373 \text{ K}} \\ = 109 \text{ J/K}$$

OR

The temperature for the phase change:

$$T = \frac{\Delta H}{\Delta S}$$

