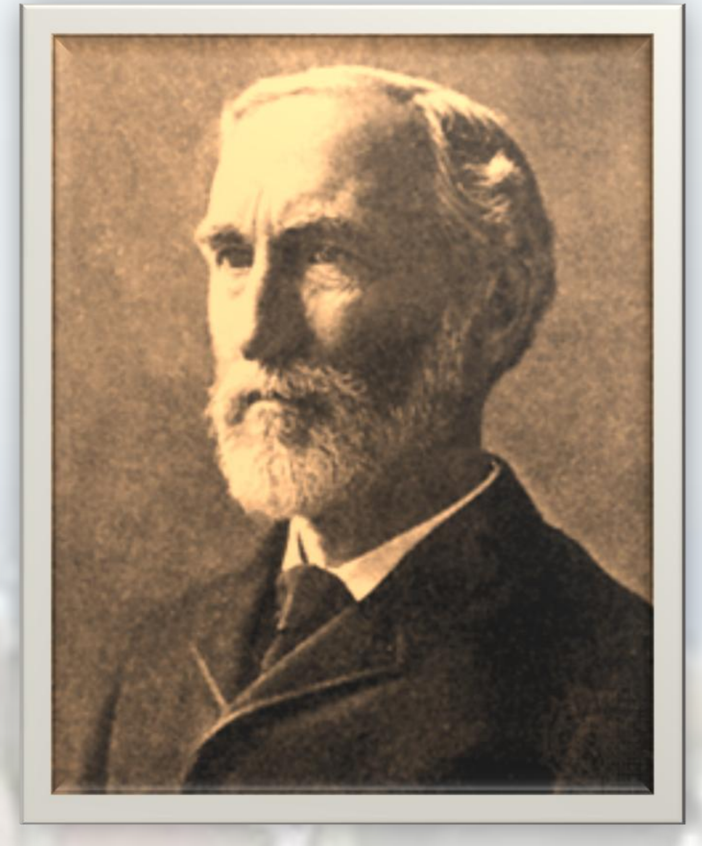
Gibbs Free Energy

Enthalpy

vs

Entropy

History



- In the 1870’s, J. W. Gibbs developed the concept of “available energy” for a chemical reaction.
- Today it is called **Gibbs energy**, **Gibbs function**, or **Gibbs Free Energy**.
- It takes into account both the entropy and the enthalpy.

Some Analogies

Entropy [disorder]	Enthalpy [potential energy]
• After a busy day of grazing in the pasture, cattle need to be rounded up.	• Before you can enjoy the thrill of a roller coaster, the car needs to get to the top.
• It takes a lot of work to round up the cattle.	• It takes a lot of work to push the car uphill.
• Open the door to the barn, and the cattle will spread themselves out. No work!!	• Get to the top of the hill, and the car will rush down by itself. No work!!
• **Conclusion: Decreasing entropy takes work. Increasing entropy releases energy.**	• **Conclusion: Increasing enthalpy takes work. Decreasing enthalpy releases energy.**

Processes in which the entropy increases and the enthalpy decreases occur spontaneously.

Entropy and Enthalpy

- Whether a reaction proceeds spontaneously or not depends on the balance between two natural tendencies:
  - The drive toward greater stability (reduced potential energy or enthalpy); and
  - The drive toward less organization (increased entropy).

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- In nature, systems tend toward
  - the lowest possible energy or enthalpy (H); and
  - toward greater randomness (disorder) or entropy (S).

The Gibbs Equation

- The Gibbs free energy change (ΔG) predicts whether or not a reaction is spontaneous.
- It takes into account
  - the change in enthalpy (ΔH); and
  - the change in entropy (ΔS).
- The Gibbs free energy change is the difference between the energy change (ΔH) and the product of the absolute or Kelvin temperature (T) and the entropy change (ΔS).

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$$\boxed{\Delta G = \Delta H - T\Delta S}$$

Applying the Gibbs Equation

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- For a system at equilibrium, $\Delta G = 0$.
- In order for a system to change spontaneously, the resulting ΔG must be negative.
- If the drive toward lower energy and higher entropy cannot be satisfied at the same time, the type of change that will be favored will depend on the temperature.
  - At low temperatures, the term $T\Delta S$ will be small, and ΔH will have the greatest effect on the free energy.
  - At high temperatures, the term $T\Delta S$ will be large, and ΔS will have the greatest effect on the free energy.

Interpreting the Gibbs Equation

Reaction Conditions			Is the reaction spontaneous? (Yes, No, Likely, or Unlikely)
Temperature	ΔH	ΔS	
High	+	–	No
High	+	+	Likely
High	–	–	Unlikely
High	–	+	Yes
Low	+	–	No
Low	+	+	Unlikely
Low	–	–	Likely
Low	–	+	Yes

An Example

- When water freezes entropy and enthalpy decrease.
- When water boils entropy and enthalpy increase.
- Water freezes at low temperature and boils at high temperature. Explain this based on the Gibbs free energy.
    - At low temperature **$T\Delta S$** is small, so it is outweighed by the negative **ΔH** when water freezes.
    - At high temperature **$T\Delta S$** is large, so it outweighs the positive **ΔH** when water boils.

Gibbs Sample Calculation

- Data for the heat of formation ($\Delta H_f°$) and free energy of formation ($\Delta G_f°$) can be found on the reference table, Table W.
- **Find the entropy of formation of carbon dioxide.**
  - Data from the table: $\Delta G_f° = -394.2$ kJ/mol; $\Delta H_f° = -393.3$ kJ/mol; T = 298K
  - $\Delta G = \Delta H - T\Delta S$
  - $-394.2 \text{ kJ/mol} = -393.3 \text{ kJ/mol} - 298\text{K}(\Delta S)$
  - $-0.9 \text{ kJ/mol} = -298\text{K}(\Delta S)$
  - $\Delta S = 0.003 \text{ kJ/mol}\bullet\text{K}$

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