4.6: Gibbs Energy

Gibbs energy is the energy of a chemical reaction that can be used to do non-mechanical work. Gibbs Energy is described as

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Where H is enthalpy, T is temperature, and S is entropy. ΔG is used to predict spontaneity within a system by

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Gibbs energy was developed in the 1870's by Josiah Willard Gibbs. He originally termed this energy as the "available energy" in a system. His paper published in 1873, "Graphical Methods in the Thermodynamics of Fluids," outlined how his equation could predict the behavior of systems when they are combined.

At a constant temperature and pressure, the Gibbs Energy of a system can be described as

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This equation can be used to determine the spontaneity of the process.

- If $\Delta G_{sys} \leq 0$, the process is spontaneous.
- If $\Delta G_{sys} = 0$, the system is at equilibrium.
- If $\Delta G_{sys} > 0$, the process is not spontaneous.

Furthermore,

- If $\Delta G_{sys} < 0$, the process is *exergonic*
- If $\Delta G_{sys} > 0$, the process is *endergonic*.

Gibbs Energy is a useful tool to describe in what manner the reaction is conducted. If ΔH >> TΔS, the reaction is enthalpy driven. However, if TΔS >> ΔH, the reaction is driven by entropy. The Clausius-Clapeyron Equation is an application derived from Gibb's energy:

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Another important application of Gibb's energy is the Maxwell relations (also available in a link at the end of the wiki page.)

Temperature & Pressure Dependence

When the pressure & temperature of a reaction are not held constant,

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For an infinitesimal process,

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For a reaction where temperature is held constant,

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From the First Law of Thermodynamics, we know

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Since

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We find that

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showing the obvious dependence of ΔG on temperature and pressure. To observe the change in Gibbs energy due to <u>temperature change alone</u> (pressure held constant) the equation becomes

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Solving for S and plugging it into Eq. (1), the Gibbs-Helmholtz Equation is found:

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The Gibbs-Helmholtz Equation is very important because it relates the change in Gibbs energy to its temperature dependence, and the position of equilibrium to change in enthalpy.

To observe the change in Gibbs energy due to <u>pressure change alone</u> (temperature held constant) the equation becomes

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If the gas is assumed to be ideal then

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for an initial and final pressure (P1 and P2) at a constant T.

Standard-State Free Energy of Formation

Gibbs Energy is defined as a state function (a property that depends only on conditions describing the system, not how the change occurs as in a path function.) This is because each component of the equation (H,T, and S) are all state functions. Therefore, we can know the change in Gibbs energy without knowing every detail of the process. In a process that takes place at constant temperature and pressure (298 K, 1 atm) the standard molar free energy of formation can be determined by the change in free energy from the reactants and products. Using predetermined values, Eqn. (17) can be used

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Standard-State Free Energy of Reaction

Gibbs Energy can be found at standard-state conditions using

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$\Delta H°$ and $\Delta S°$ values can be found in the appendix of any general chemistry textbook, or using this link.

Free Energy of Reaction

Gibbs energy can be found at any conditions by relating it to the standard-state free energy of reaction, using

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Where Q is the reaction quotient. Very rarely does chemistry actually occur at the given "standard-state" conditions. Using the above equation and standard-state values, chemists can determine the overall Gibb's energy for the system, regardless of the conditions.

References

1. Olmsted, J. *Chemistry*, 4th ed.; John Wiley & Sons, Inc: Hoboken 2006.
2. Chang, R. *Physical Chemistry for the Biosciences*; University Science Books: Sausalito, 2005.
3. Christian, S.D. Gibbs-Duhem equation and free energy calculations. *J. Chem. Educ.* **1962,** *39 (10)* 521-524.
4. Porter, S.K. The volume-entropy-energy surface of J.W. Gibbs. *J. Chem Educ.* **1971,** *48(4)* 231-234.

Problems

1. Calculate the standard-state free energy of formation for the $H_2O_2(l)$ from H_2 and O_2, given the following values:
   Δ_fG (H_2): 0 kJ/mol
   Δ_fG (O_2): 0 kJ/mol
   Δ_fG ($H_2O_2(l)$): -120.4 kJ/mol

   Hint: (product*coefficient) - [(Reactant1*coefficient)+(Reactant2*coefficient)]
2. Consider the following reaction: *[Math Processing Error]*
   At what temperature will this reaction become favorable? Note: Assume $\Delta H_r°$ and $\Delta S_r°$ are temperature independent.
   Given values:

Substance	$\Delta H_f°$	$S_f°$

Substance	$\Delta H_f°$	$S_f°$
$CaCO_3$	-1206.9 kJ/mol	92.9 J/K mol
CaO	-635.6 kJ/mol	39.8 J/K mol
CO_2	-393.5 kJ/mol	213.6 J/K mol

Hint: At what value of ΔG does a reaction become spontaneous, and therefore favorable? Next, find the ΔH value for the reaction (products-reactants) and the ΔS values for the reaction (products-reactants.) Solve for T.

3. Is the above decomposition of calcium carbonate enthalpy driven or entropy driven?

Hint: Is ΔH >> TΔS, or TΔS >> ΔH?

Anwers to Problems

1. -120.4 kJ/mol
2. 1107.8 K
3. Enthalpy

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