

4.8: Dependence of Gibbs Energy on Temperature and Pressure

Learning Objectives

- To get an overview of Gibbs energy and its general uses in chemistry.
 - Understand how Gibbs energy pertains to reactions properties
 - Understand how Gibbs energy pertains to equilibria properties
 - Understand how Gibbs energy pertains to electrochemical properties

Gibbs free energy, denoted ΔG , combines enthalpy and entropy into a single value. The change in free energy, ΔG , is equal to the sum of the enthalpy plus the product of the temperature and entropy of the system. ΔG can predict the direction of the chemical reaction under two conditions:

1. constant temperature and
2. constant pressure.

If ΔG is positive, then the reaction is nonspontaneous (i.e., an the input of external energy is necessary for the reaction to occur) and if it is negative, then it is spontaneous (occurs without external energy input).

Introduction

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. This quantity is the energy associated with a chemical reaction that can be used to do work, and is the sum of its enthalpy (H) and the product of the temperature and the entropy (S) of the system. This quantity is defined as follows:

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

or more completely as

$$\Delta G = \Delta H - T\Delta S + P\Delta V$$

where

- ΔU is internal energy (SI unit: joule)
- P is pressure (SI unit: pascal)
- V is volume (SI unit: m^3)
- T is temperature (SI unit: kelvin)
- S is entropy (SI unit: joule/kelvin)
- H is the enthalpy (SI unit: joule)

Gibbs Energy in Reactions

Spontaneous - is a reaction that is consider to be natural because it is a reaction that occurs by itself without any external action towards it. Non spontaneous - needs constant external energy applied to it in order for the process to continue and once you stop the external action the process will cease. When solving for the equation, if change of G is negative, then it's spontaneous. If change of G if positive, then it's non spontaneous. The symbol that is commonly used for FREE ENERGY is G. can be more properly consider as "standard free energy change"

In chemical reactions involving the changes in thermodynamic quantities, a variation on this equation is often encountered:

$$\Delta G = \Delta H - T\Delta S + P\Delta V$$

✓ Example 1.1

Calculate ΔG at 290 K for the following reaction:



Given

- $\Delta H = -120 \text{ kJ}$
- $\Delta S = -150 \text{ JK}^{-1}$

Solution

now all you have to do is plug in all the given numbers into Equation 3 above. Remember to divide ΔH by 1000 so that after you multiply by temperature, it will have the same units, as ΔS .

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

and substituting into Equation 3:

$\Delta G = -120 \text{ kJ} - (-150 \text{ JK}^{-1})(298 \text{ K})$

? Exercise 1.1: The Haber Process

What is the ΔG for this formation of ammonia from nitrogen and hydrogen gas.

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

The Standard free energy formations: $\text{NH}_3 = -16.45 \text{ kJ/mol}$ $\text{H}_2 = 0$ $\text{N}_2 = 0$

Answer

$\Delta G = -16.45 \text{ kJ/mol}$

Since the changes of entropy of chemical reaction are not measured readily, thus, entropy is not typically used as a criterion. To obviate this difficulty, we can use ΔG . The sign of ΔG indicates the direction of a chemical reaction and determine if a reaction is spontaneous or not.

- $\Delta G < 0$: reaction is spontaneous in the direction written (i.e., the reaction is **exergonic**)
- $\Delta G = 0$: the system is at equilibrium and there is no net change either in forward or reverse direction.
- $\Delta G > 0$: reaction is not spontaneous and the process proceeds spontaneously in the reverse direction. To drive such a reaction, we need to have input of free energy (i.e., the reaction is **endergonic**)

The factors affect ΔG of a reaction (assume ΔH and ΔS are independent of temperature):

ΔH	ΔS	ΔG	Example
+	+	at low temperature: +, at high temperature: -	$2\text{HgO}(s) \rightarrow 2\text{Hg}(l) + \text{O}_2(g)$
+	-	at all temperature: +	$3\text{O}_2(g) \rightarrow 2\text{O}_3(g)$
-	+	at all temperature: -	$2\text{H}_2\text{O}_2(l) \rightarrow 2\text{H}_2\text{O}(l) + \text{O}_2(g)$
-	-	at low temperature: -, at high temperature: +	$\text{NH}_3(g) + \text{HCl}(g) \rightarrow \text{NH}_4\text{Cl}(s)$

Note:

1. ΔG depends only on the difference in free energy of products and reactants (or final state and initial state). ΔG is independent of the path of the transformation and is unaffected by the mechanism of a reaction.
2. ΔG cannot tell us anything about the rate of a reaction.

The standard Gibbs energy change ΔG° (at which reactants are converted to products at 1 bar) for:

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

$\Delta G^\circ = -120 \text{ kJ} - (-150 \text{ JK}^{-1})(298 \text{ K})$

$\Delta G^\circ = -120 \text{ kJ} + 44.7 \text{ kJ} = -75.3 \text{ kJ}$

The standard-state free energy of reaction ($\Delta_r G^\circ$) is defined as the free energy of reaction at standard state conditions:

$$\Delta_r G^\circ = \sum \nu_i \Delta_f G^\circ(\text{products}) - \sum \nu_j \Delta_f G^\circ(\text{reactants})$$

Note

- If $\Delta_r G^\circ < 0$: the reaction is *enthalpy-driven*
- If $\Delta_r G^\circ > 0$ & $T\Delta_r S^\circ > \Delta_r H^\circ$: the reaction is *entropy-driven*

Standard-State Free Energy of Formation

- The partial pressure of any gas involved in the reaction is 0.1 MPa.
- The concentrations of all aqueous solutions are 1 M.
- Measurements are generally taken at a temperature of 25° C (298 K).

The standard-state free energy of formation is the change in free energy that occurs when a compound is formed from its elements in their most thermodynamically stable states at standard-state conditions. In other words, it is the difference between the free energy of a substance and the free energies of its constituent elements at standard-state conditions:

$$\Delta_f G^\circ = G^\circ(\text{compound}) - \sum G^\circ(\text{elements})$$

Example 1.2

Used the below information to determine if CaCO_3 will dissolve in water at room temperature.

Compound	$\Delta_f G^\circ$	$\Delta_f H^\circ$
CaCO_3	-365.56	151.08
Ca^{2+}	-132.51	113.4
CO_3^{2-}	205.0	146.4

Solution

This question is essentially asking if the following reaction is spontaneous at room temperature.



This would normally only require calculating $\Delta_r G^\circ$ and evaluating its sign. However, the $\Delta_f G^\circ$ values are not tabulated, so they must be calculated manually from calculated $\Delta_f H^\circ$ and $\Delta_f S^\circ$ values for the reaction.

- Calculate $\Delta_f S^\circ$:

$$\Delta_f S^\circ(\text{CaCO}_3) = S^\circ(\text{CaCO}_3) - S^\circ(\text{Ca}) - \frac{3}{2} S^\circ(\text{O}_2)$$

$$\Delta_f S^\circ(\text{Ca}^{2+}) = S^\circ(\text{Ca}^{2+}) - S^\circ(\text{Ca})$$

$$\Delta_f S^\circ(\text{CO}_3^{2-}) = S^\circ(\text{CO}_3^{2-}) - S^\circ(\text{C}) - 3 S^\circ(\text{O}_2)$$

$$\Delta_r S^\circ = \Delta_f S^\circ(\text{Ca}^{2+}) + \Delta_f S^\circ(\text{CO}_3^{2-}) - \Delta_f S^\circ(\text{CaCO}_3)$$

- Calculate $\Delta_f H^\circ$:

$$\Delta_f H^\circ(\text{CaCO}_3) = H^\circ(\text{CaCO}_3) - H^\circ(\text{Ca}) - \frac{3}{2} H^\circ(\text{O}_2)$$

$$\Delta_f H^\circ(\text{Ca}^{2+}) = H^\circ(\text{Ca}^{2+}) - H^\circ(\text{Ca})$$

$$\Delta_f H^\circ(\text{CO}_3^{2-}) = H^\circ(\text{CO}_3^{2-}) - H^\circ(\text{C}) - 3 H^\circ(\text{O}_2)$$

$$\Delta_r H^\circ = \Delta_f H^\circ(\text{Ca}^{2+}) + \Delta_f H^\circ(\text{CO}_3^{2-}) - \Delta_f H^\circ(\text{CaCO}_3)$$

- Calculate $\Delta_r G^\circ$:

These values can be substituted into the free energy equation

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

Plug in [Math Processing Error], [Math Processing Error] and [Math Processing Error] into Equation 1.7

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

This reaction is spontaneous at room temperature since [Math Processing Error] is negative. Therefore [Math Processing Error] will dissolve in water at room temperature.

✓ Example 1.3

Calculate [Math Processing Error] for the following reaction at [Math Processing Error]. Will the reaction occur spontaneously?

[Math Processing Error]

given for the reaction

- [Math Processing Error]
- [Math Processing Error]

Solution

calculate [Math Processing Error] from the formula

[Math Processing Error]

but first we need to convert the units for [Math Processing Error] into kJ/K (or convert [Math Processing Error] into J) and temperature into Kelvin

- [Math Processing Error]
- [Math Processing Error]

The definition of Gibbs energy can then be used directly

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

Yes, this reaction is spontaneous at room temperature since [Math Processing Error] is negative.

Gibbs Energy in Equilibria

Let's consider the following reversible reaction:

[Math Processing Error]

The following equation relates the standard-state free energy of reaction with the free energy at any point in a given reaction (not necessarily at standard-state conditions):

[Math Processing Error]

- [Math Processing Error] = free energy at any moment
- [Math Processing Error] = standard-state free energy
- R is the ideal gas constant = 8.314 J/mol-K

- T is the absolute temperature (Kelvin)
- $\ln Q$ is natural logarithm of the **reaction quotient**

At equilibrium, $\Delta G = 0$ and $Q=K$. Thus the equation can be arranged into:

$$\Delta G^\circ = -RT \ln K$$

with

- ΔG° = standard free energy change
- R = gas constant = $1.98 \times 10^{-3} \text{ kcal mol}^{-1} \text{ deg}^{-1}$
- T = is usually room temperature = 298 K
- Q = reaction quotient

The Gibbs free energy ΔG depends primarily on the reactants' nature and concentrations (expressed in the $\ln Q$ term and the logarithmic term of Equation 1.11, respectively).

At equilibrium, ΔG : no driving force remains

$$\Delta G = 0$$

$$\Delta G^\circ = -RT \ln K$$

The equilibrium constant is defined as

$$K = \frac{[\text{products}]}{[\text{reactants}]}$$

When ΔG° is large, almost all reactants are converted to products. Substituting $\Delta G^\circ = -RT \ln K$ into Equation 1.14, we have:

$$\Delta G^\circ = -RT \ln K$$

or

$$\ln K = \frac{-\Delta G^\circ}{RT}$$

Rearrange,

$$\Delta G^\circ = -RT \ln K$$

This equation is particularly interesting as it relates the free energy difference under standard conditions to the properties of a system at equilibrium (which is rarely at standard conditions).

Table 1.1: Converting ΔG° to $\ln K$

ΔG° (kcal/mol)	$\ln K$
6.82	6.82
5.46	5.46
4.09	4.09
2.73	2.73
1.36	1.36
1	0
-1.36	-1.36
-2.73	-2.73
-4.09	-4.09
-5.46	-5.46
-6.82	-6.82

✓ Example 1.4

What is *[Math Processing Error]* for isomerization of dihydroxyacetone phosphate to glyceraldehyde 3-phosphate?

If at equilibrium, we have *[Math Processing Error]* at 298 K and pH 7. We can calculate:

$$[Math Processing Error]$$

Given:

- The initial concentration of dihydroxyacetone phosphate = *[Math Processing Error]*
- The initial concentration of glyceraldehyde 3-phosphate = *[Math Processing Error]*

Solution

From equation 2:

$$[Math Processing Error] = 1.8 \text{ kcal/mol} + 2.303 RT \log_{10}(3 \cdot 10^{-6} \text{ M} / 2 \cdot 10^{-4} \text{ M}) = -0.7 \text{ kcal/mol}$$

📌 Note

Under non-standard conditions (which is essential all reactions), the spontaneity of reaction is determined by *[Math Processing Error]*, not *[Math Processing Error]*.

Gibbs Energy in Electrochemistry

The [Nernst equation](#) relates the standard-state cell potential with the cell potential of the cell at any moment in time:

$$[Math Processing Error]$$

with

- *[Math Processing Error]* = cell potential in volts (joules per coulomb)
- *[Math Processing Error]* = moles of electrons
- *[Math Processing Error]* = Faraday's constant: 96,485 coulombs per mole of electrons

By rearranging this equation we obtain:

$$[Math Processing Error]$$

multiply the entire equation by *[Math Processing Error]*

$$[Math Processing Error]$$

which is similar to:

$$[Math Processing Error]$$

By juxtaposing these two equations:

$$[Math Processing Error]$$

$$[Math Processing Error]$$

it can be concluded that:

$$[Math Processing Error]$$

Therefore,

$$[Math Processing Error]$$

📌 Some remarks on the Gibbs "Free" Energy

- **Free Energy is not necessarily "free"**: The appellation "free energy" for G has led to so much confusion that many scientists now refer to it simply as the Gibbs energy. The "free" part of the older name reflects the steam-engine origins of thermodynamics with its interest in converting heat into work: ΔG is the maximum amount of energy which can be "freed" from the system to perform useful work. By "useful", we mean work other than that which is associated with the expansion

of the system. This is most commonly in the form of electrical work (moving electric charge through a potential difference), but other forms of work (osmotic work, increase in surface area) are also possible.

- **Free Energy is not energy:** A much more serious difficulty with the Gibbs function, particularly in the context of chemistry, is that although G has the units of energy (joules, or in its intensive form, J mol^{-1}), it lacks one of the most important attributes of energy in that it is not conserved. Thus although the free energy always falls when a gas expands or a chemical reaction takes place spontaneously, there need be no compensating increase in energy anywhere else. Referring to G as an energy also reinforces the false but widespread notion that a fall in energy must accompany any change. But if we accept that energy is conserved, it is apparent that the only necessary condition for change (whether the dropping of a weight, expansion of a gas, or a chemical reaction) is the redistribution of energy. The quantity $-\Delta G$ associated with a process represents the quantity of energy that is “shared and spread”, which as we have already explained is the meaning of the increase in the entropy. The quotient $-\Delta G/T$ is in fact identical with ΔS_{total} , the entropy change of the world, whose increase is the primary criterion for any kind of change.
- **Free Energy is not even "real":** G differs from the thermodynamic quantities H and S in another significant way: it has no physical reality as a property of matter, whereas H and S can be related to the quantity and distribution of energy in a collection of molecules (e.g., [the third law of thermodynamics](#)). The free energy is simply a useful construct that serves as a criterion for change and makes calculations easier.

References

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