

9.1: Gibbs Equation

Recalling from chapter 8, the definition of G is:

$$G = U - TS + PV = H - TS,$$

which, taking the differential at constant T and P , becomes:

$$dG = dH - \overbrace{SdT}^{=0} - TdS = dH - TdS.$$

Integrating Equation 9.1.1 between the initial and final states of a process results in:

$$\int_i^f dG = \int_i^f dH - T \int_i^f dS \quad (9.1.1)$$

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

which is the famous **Gibbs equation** for ΔG . Using [Definition: Spontaneous Process](#), we can use ΔG to infer the spontaneity of a chemical process that happens at constant T and P using $\Delta G \leq 0$. If we set ourselves at standard conditions, we can calculate the standard Gibbs free energy of formation, $\Delta_{\text{rxn}} G^\ominus$, for any reaction as:

$$\begin{aligned} \Delta_{\text{rxn}} G^\ominus &= \Delta_{\text{rxn}} H^\ominus - T \Delta_{\text{rxn}} S^\ominus \\ &= \sum_i \nu_i \Delta_f H_i^\ominus + T \sum_i \nu_i S_i^\ominus, \end{aligned}$$

where $\Delta_f H_i^\ominus$ are the standard enthalpies of formation, S_i^\ominus are the standard entropies, and ν_i are the stoichiometric coefficients for every species i involved in the reaction. All these quantities are commonly available, and we have already discussed their usage in [chapters 4](#) and [7](#), respectively.¹

The following four options are possible for ΔG^\ominus of a chemical reaction:

ΔG^\ominus		ΔH^\ominus	ΔS^\ominus	Spontaneous?
–	if	–	+	Always
+	if	+	–	Never
–/+	if	–	–	Depends on T : spontaneous at low T
+/–	if	+	+	Depends on T : spontaneous at high T

Or, in other words:

- Exothermic reactions that increase the entropy are always spontaneous.
- Endothermic reactions that reduce the entropy are always non-spontaneous.
- For the other two cases, the spontaneity of the reaction depends on the temperature:
 - Exothermic reactions that reduce the entropy are spontaneous at low T .
 - Endothermic reactions that increase the entropy are spontaneous at high T .

A simple criterion to evaluate the entropic contribution of a reaction is to look at the total number of moles of the reactants and the products (as the sum of the stoichiometric coefficients). If the reaction is producing more molecules than it destroys ($|\sum_{\text{products}} \nu_i| > |\sum_{\text{reactants}} \nu_i|$), it will increase the entropy. Vice versa, if the total number of moles in a reaction is reducing ($|\sum_{\text{products}} \nu_i| < |\sum_{\text{reactants}} \nu_i|$), the entropy will also reduce.

As we saw in [section 8.2](#), the natural variables of the Gibbs free energy are the temperature, T , the pressure, P , and chemical composition, as the number of moles $\{n_i\}$. The Gibbs free energy can therefore be expressed using the total differential as (see

also, last formula in Equation 8.4.2):

$$dG(T, P, \{n_i\}) = \underbrace{\left(\frac{\partial G}{\partial T}\right)_{P, \{n_i\}} dT}_{\text{temperature dependence}} + \underbrace{\left(\frac{\partial G}{\partial P}\right)_{T, \{n_i\}} dP}_{\text{pressure dependence}} + \sum_i \underbrace{\left(\frac{\partial G}{\partial n_i}\right)_{T, P, \{n_{j \neq i}\}} dn_i}_{\text{composition dependence}}. \quad (9.1.2)$$

If we know the behavior of G as we vary each of the three natural variables independently of the other two, we can reconstruct the total differential dG . Each of these terms represents a coefficient in Equation 9.1.2, which are given in Equation 8.4.3.

1. It is not uncommon to see values of $\Delta_f G^\ominus$ tabulated alongside $\Delta_f H^\ominus$ and S_i^\ominus , which simplifies even further the calculation. In fact, a comprehensive list of standard Gibbs free energy of formation of inorganic and organic compounds is reported in the appendix of this book 16. For cases where $\Delta_f G^\ominus$ are not reported, they can always be calculated by their constituents.

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