

8.3: Free Energies

The Legendre transformation procedure translates all information contained in the original function to the new one. Therefore, $H(S, P, \{n_i\})$, $A(T, V, \{n_i\})$, and $G(T, P, \{n_i\})$ all contain the same information that is in $U(S, V, \{n_i\})$. However, the new functions depend on different natural variables, and they are useful at different conditions. For example, when we want to study chemical changes, we are interested in studying the term $\sum_i \mu_i dn_i$ that appears in each thermodynamic potential. To do so, we need to isolate the chemical term by keeping all other natural variables constant. For example, changes in the chemical term will correspond to changes in the internal energy at constant S and constant V :

$$dU(S, V, \{n_i\}) = \sum_i \mu_i dn_i \quad \text{if} \quad dS = dV = 0. \quad (8.3.1)$$

Similarly:

$$\begin{aligned} dH(S, P, \{n_i\}) &= \sum_i \mu_i dn_i \quad \text{if} \quad dS = dP = 0, \\ dA(T, V, \{n_i\}) &= \sum_i \mu_i dn_i \quad \text{if} \quad dT = dV = 0, \\ dG(T, P, \{n_i\}) &= \sum_i \mu_i dn_i \quad \text{if} \quad dT = dP = 0. \end{aligned} \quad (8.3.2)$$

The latter two cases are particularly interesting since most of chemistry happens at either constant volume,¹ or constant pressure.² Since $dS = 0$ is not a requirement for both free energies to describe chemical changes, we can apply either of them to study non-isentropic processes. If a process is not isentropic, it either increases the entropy of the universe, or it decreases it. Therefore—according to the second law—it is either spontaneous or not. Using this concept in conjunction with Clausius theorem, we can devise new criteria for inferring the spontaneity of a process that depends exclusively on the free energies.

Recalling Clausius theorem:

$$dS^{\text{sys}} \geq \frac{dQ}{T_{\text{surr}}} \quad \longrightarrow \quad TdS \geq dQ, \quad (8.3.3)$$

we can consider the two cases: constant V ($dQ_V = dU$, left), and constant P ($dQ_P = dH$, right):

constant V :	constant P :
$TdS \geq dU$	$TdS \geq dH$
$TdS - dU \geq 0$	$TdS - dH \geq 0$

(8.3.4)

we can then simplify the definition of free energies, eqs. 8.2.4 and 8.2.6:

constant T, V :	constant T, P :
$(dA)_{T,V} = dU - TdS$	$(dG)_{T,P} = dH - TdS$
$dU = (dA)_{T,V} + TdS$	$dH = (dG)_{T,P} + TdS$

(8.3.5)

and by merging dU and dH from eqs. 8.3.5 into Clausius theorem expressed using eqs. 8.3.4, we obtain:

$TdS - (dA)_{T,V} - TdS \geq 0$	$TdS - (dG)_{T,P} - TdS \geq 0$
$(dA)_{T,V} \leq 0$	$(dG)_{T,P} \leq 0.$

(8.3.6)

These equations represent the conditions on dA and dG for inferring the spontaneity of a process, and can be summarized as follows:

Definition: Spontaneous Process

During a spontaneous process at constant temperature and volume, the Helmholtz free energy will decrease ($dA < 0$), until it reaches a stationary point at which the system will be at equilibrium ($dA = 0$).

During a spontaneous process at constant temperature and pressure, the Gibbs free energy will decrease ($dG < 0$), until it reaches a stationary point at which the system will be at equilibrium ($dG = 0$).

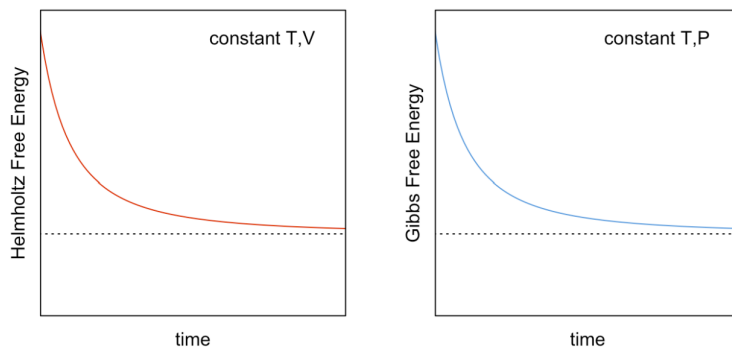


Figure 8.3.1: Behavior of Helmholtz (red) and Gibbs (blue) Free Energies for Spontaneous Processes at Constant T, V (left) and Constant T, P (right).

1. for example, several industrial processes in chemical plants.
2. for example, most processes in a chemistry lab.

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