6.1: Free Energy Functions

In the previous chapter, we saw that for a spontaneous process, $\Delta S_{universe} > 0$. While this is a useful criterion for determining whether or not a process is spontaneous, it is rather cumbersome, as it requires one to calculate not only the entropy change for the system, but also that of the surroundings. It would be much more convenient if there was a single criterion that would do the job and focus only on the system. As it turns out, there is.

Since we know that

$$\Delta S_{univ} \geq 0$$

for any natural process, and

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$$

all we need to do is to find an expression for ΔS_{sys} that can be determined by the changes in the system itself. Fortunately, we have already done that! Recalling that at constant temperature

$$\Delta S = -\frac{q_{rev}}{T}$$

and at constant pressure

$$\Delta H = q_p$$

it follows that at constant temperature and pressure

$$\Delta S_{surr} = -\frac{\Delta H_{sys}}{T}$$

Substitution into the above equations yields an expression for the criterion of spontaneity that depends only on variables describing the changes in the system!

$$\Delta S_{univ} \geq \Delta S_{sys} - \frac{\Delta H_{sys}}{T}$$

so

$$\Delta S_{sys} - \frac{\Delta H_{sys}}{T} \geq 0$$

Multiplying both sides by $-T$ yields

$$\Delta H - T\Delta S \leq 0 \tag{6.1.1}$$

A similar derivation for constant volume processes results in the expression (at constant volume and temperature)

$$\Delta U - T\Delta S \leq 0 \tag{6.1.2}$$

> Equation 6.1.1 is of great use to chemists, as most of chemistry occurs at constant pressure. For geologists, however, who are interested in processes that occur at very high pressures (say, under the weight of an entire mountain) and expansion is not a possibility, the constant volume expression of Equation 6.1.1 may be of greater interest.

All of the above arguments can be made for systems in which the temperature is not constant by considering infinitesimal changes. The resulting expressions are

$$dH - TdS \leq 0 \tag{6.1.3}$$

and

$$dU - TdS \leq 0 \tag{6.1.4}$$

The Gibbs and Helmholtz Functions

Equation 6.1.3 suggests a very convenient thermodynamic function to help keep track of both the effects of entropy and enthalpy changes. This function, the **Gibbs function** (or **Gibbs Free Energy**) is defined by

$$G \equiv H - TS$$

A change in the Gibbs function can be expressed

$$\Delta G = \Delta H - \Delta(TS)$$

Or at constant temperature

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

And the criterion for a process to be spontaneous is the DG < 0. As such, it should be clear spontaneity is not merely a function the enthalpy change (although exothermic processes tend to be spontaneous) but also a function of the entropy change, weighted by the temperature. Going back to an earlier example,

$$NaOH(s) \rightarrow Na^+(aq) + OH^-(aq)$$

with $\Delta H < 0$.

and

$$NaHCO_3(s) \rightarrow Na^+(aq) + HCO_3^-(aq)$$
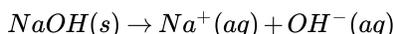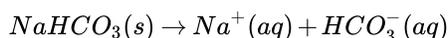
with $\Delta H > 0$.

It is easy to see why both processes are spontaneous. In the first case, the process is exothermic (favorable) and proceeds with an increase in entropy (also favorable) due to the formation of fragments in the liquid phase (more chaotic) from a very ordered solid (more ordered). The second reaction is endothermic (unfavorable) but proceeds with an increase in entropy (favorable). So, so long as the temperature is high enough, the entropy term will overwhelm the enthalpy term and cause the process to be spontaneous. The conditions for spontaneous processes at constant temperature and pressure can be summarized in Table 6.1.1.

Table 6.1.1: Spontaneity Conditions for a Process under Constant Temperature and Pressure

ΔH	ΔS	Spontaneous
> 0	> 0	At high T
> 0	< 0	At no T
< 0	> 0	At all T
< 0	< 0	At low T

Similarly to the Gibbs function, the **Helmholtz function** is defined by

$$A \equiv U - TS$$

and provides another important criterion for spontaneous processes at constant value and temperature. *At constant temperature*, the Helmholtz function can be expressed by

$$\Delta A \equiv \Delta U - T\Delta S$$

Based on similar arguments used for the Gibbs function, the Helmholtz function also can be used to predict which processes will be spontaneous at constant volume and temperature according to Table 6.1.2.

Table 6.1.2: Spontaneity Conditions for a Process under Constant Temperature and Volume

ΔU	ΔS	Spontaneous?
> 0	> 0	At high T
> 0	< 0	At no T

ΔU	ΔS	Spontaneous?
< 0	> 0	At all T
< 0	< 0	At low T

Calculating ΔG for Reactions

Much like in the case of enthalpy (and unlike entropy), free energy functions do not have an unambiguous zero to the energy scale. So, just like in the case of enthalpies of formation, by convention, the standard free energy of formation (ΔG_f^o) for elements in their standard states is defined as zero. This allows for two important things to happen. First, ΔG_f^o can be measured and tabulated for any substance (in principle, at least.) ΔG_f^o is determined to be ΔG_{rxn}^o for the reaction that forms one mole of a compound from elements in their standard states (similarly to how ΔH_f^o is defined.) Secondly, tabulated (ΔG_f^o) can be used to calculate standard reaction free energies (ΔG_{rxn}^o) in much the same way as ΔH_f^o is used for reaction enthalpies.
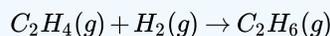
> ✔ Example 6.1.1:
>
> Given the following data at 298 K, calculate ΔG^o at 298 K for the following reaction:
>
> $$C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$$
>
> | Substance | ΔG_f^o (kJ/mol) |
> |---|---|
> | C_2H_4(g) | 68.4 |
> | C_2H_6(g) | -32.0 |
>
> **Solution**
>
> The ΔG_f^o values can be used to calculate ΔG^o for the reaction in exactly the same method as ΔH_f^o can be used to calculate a reaction enthalpy.
>
> $$\Delta G^o = (1\ mol)(-32.0\ kJ/mol) - (1\ mol)(68.4\ kJ/mol)$$
>
> $$\Delta G^o = 100.4\ kJ$$
>
> *Note*: $H_2(g)$ is not included in the calculation since ΔG_f^o for $H_2(g)$ is 0 since it is an element in its standard state.