

Chemistry 331

Lecture 12 Free Energy Functions

NC State University

System and surroundings both play in role in the entropy

In an isolated system the criterion $dS > 0$ indicates that a process is spontaneous. In general, we must consider dS_{sys} for the system and dS_{surr} for surroundings. Since we can think of the entire universe as an isolated system $dS_{\text{total}} > 0$. The entropy tends to increase for the universe as a whole. If we decompose dS_{total} into the entropy change for the system and that for the surroundings we have a criterion for spontaneity for the system that also requires consideration of the entropy change in the surroundings. The free energy functions will allow us to eliminate consideration of the surroundings and to express a criterion for spontaneity solely in terms of parameters that depend on the system.

Free Energy at Constant T and V

Starting with the First Law

$$dU = \delta w + \delta q$$

At constant temperature and volume we have $\delta w = 0$ and

$$dU = \delta q$$

Recall that $dS \geq \delta q/T$ so we have

$$dU \leq TdS$$

which leads to

$$dU - TdS \leq 0$$

Since T and V are constant we can write this as

$$d(U - TS) \leq 0$$

The quantity in parentheses is a measure of the spontaneity of the system that depends on known state functions.

Definition of Helmholtz Free Energy

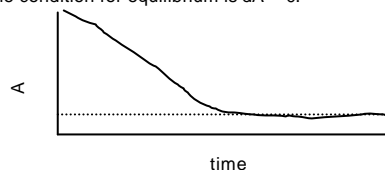
We define a new state function:

$$A = U - TS \text{ such that } dA \leq 0.$$

We call A the Helmholtz free energy.

At constant T and V the Helmholtz free energy will decrease until all possible spontaneous processes have occurred. At that point the system will be in equilibrium.

The condition for equilibrium is $dA = 0$.



Definition of Helmholtz Free Energy

Expressing the change in the Helmholtz free energy we have $\Delta A = \Delta U - T\Delta S$

for an isothermal change from one state to another.

The condition for spontaneous change is that ΔA is less than zero and the condition for equilibrium is that $\Delta A = 0$.

We write

$$\Delta A = \Delta U - T\Delta S \leq 0 \text{ (at constant T and V)}$$

If ΔA is greater than zero a process is not spontaneous.

It can occur if work is done on the system, however. The Helmholtz free energy has an important physical interpretation.

Noting the $q_{\text{rev}} = T\Delta S$ we have

$$\Delta A = \Delta U - q_{\text{rev}}$$

According to the first law $\Delta U - q_{\text{rev}} = w_{\text{rev}}$ so

$$\Delta A = w_{\text{rev}} \text{ (reversible, isothermal)}$$

A represents the maximum amount of reversible work that can be extracted from the system.

Definition of Gibbs Free Energy

Most reactions occur at constant pressure rather than constant volume.

Using the facts that $q_{\text{rev}} = TdS$ and $w_{\text{rev}} = -PdV$ we have:

$$dU \leq TdS - PdV$$

which can be written $dU - TdS + PdV \leq 0$.

The \leq sign applies to an equilibrium condition and

the $<$ sign means that the process is spontaneous. Therefore:

$$d(U - TS + PV) \leq 0 \text{ (at constant T and P)}$$

We define a state function $G = U + PV - TS = H - TS$.

Thus, $dG \leq 0$ (at constant T and P)

The quantity G is called the Gibbs free energy.

In a system at constant T and P, the Gibbs energy will decrease as the result of spontaneous processes until the system reaches equilibrium, where $dG = 0$.

Comparing Gibbs and Helmholtz

The quantity G is called the Gibb's free energy. In a system at constant T and P, the Gibb's energy will decrease as the result of spontaneous processes until the system reaches equilibrium, where $dG = 0$.

Comparing the Helmholtz and Gibb's free energies we see that A(V,T) and G(P,T) are completely analogous except that A is valid at constant V and G is valid at constant P.

We can see that

$$G = A + PV$$

which is exactly analogous to

$$H = U + PV$$

the relationship between enthalpy and internal energy.

For chemical processes we see that

$$\Delta G = \Delta H - T\Delta S \leq 0 \text{ (at constant T and P)}$$

$$\Delta A = \Delta U - T\Delta S \leq 0 \text{ (at constant T and V)}$$

Conditions for Spontaneity

We will not use the Helmholtz free energy to describe chemical processes. It is an important concept in the derivation of the Gibbs energy. However, from this point we will consider the implications of the Gibbs energy for physical and chemical processes.

There are four possible combinations of the sign of ΔH and ΔS in the Gibbs free energy change:

ΔH	ΔS	Description of process
>0	>0	Endothermic, spontaneous for $T > \Delta H/\Delta S$
<0	<0	Exothermic, spontaneous for $T < \Delta H/\Delta S$
<0	>0	Exothermic, spontaneous for all T
>0	>0	Never spontaneous

Gibbs energy for a phase change

For a phase transition the two phases are in equilibrium. Therefore, $\Delta G = 0$ for a phase transition.

For example, for water liquid and vapor are in equilibrium at 373.15 K (at 1 atm of pressure). We can write

$$D_{vap}G = G_{H_2O(g)} - G_{H_2O(l)}$$

where we have expressed G as a molar free energy.

From the definition of free energy we have

$$D_{vap}G = D_{vap}H - TD_{vap}S$$

The magnitude of the molar enthalpy of vaporization is 40.7 kJ/mol and that of the entropy is 108.9 J/mol-K.

Thus,

$$D_{vap}G = 40.65 \text{ kJ} \cdot \text{mol}^{-1} - \left\{ 373.15 \text{ K} \left[108.9 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \right] \right\} = 0$$

Gibbs energy for a phase change

However, if we were to calculate the free energy of vaporization at 363.15 K we would find that it is +1.1 kJ/mol so vaporization is not spontaneous at that temperature.

If we consider the free energy of vaporization at 383.15 K it is -1.08 kJ/mol and so the process is spontaneous ($DG < 0$).

State Function Summary

At this point we summarize the state functions that we have developed:

U (internal energy)

H = U + PV (enthalpy)

S (entropy)

A = U + TS (Helmholtz free energy)

G = U + PV + TS = H + TS (Gibbs free energy)

Please note that we can express each of these in a differential form. This simply refers to the possible changes in each function expressed in terms of its dependent variables.

$$dH = dU + PdV + VdP$$

$$dA = dU + TdS + SdT$$

$$dG = dH + TdS + SdT$$