Gibb's free energy

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

$$\Delta_{vap}G_m = G_m\left(H_2O(g)\right) - G_m\left(H_2O(l)\right)$$

where we have expressed G as a molar free energy. From the definition of free energy we have

$$\Delta_{vap}G_m = \Delta_{vap}H_m - T\Delta_{vap}S_m$$

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,

$$\Delta_{vap}\bar{G} = 40.65 \; kJ \cdot mol^{-1} - \left(373.15 \; K\right)\left(108.9 \; J \cdot K^{-1} \cdot mol^{-1}\right) = 0$$

Gibbs energy for a phase change

However, if we were to calculate the free energy of vaporization at 372.15 K we would find that it is +100 J/mol so vaporization is not spontaneous at that temperature ($\Delta G > 0$).

If we consider the free energy of vaporization at 374.15 K it is -100 J/mol and so the process is spontaneous ($\Delta G < 0$).

Thus, we see that equilibrium is defined as $\Delta G = 0$, but that temperature can cause a shift away from the position of equilibrium. At equilibrium there will be some amount of water liquid and vapor present. As we shift the temperature above or below 373.15 K, we find that the reaction favors vapor or liquid, respectively.

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)

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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

The internal energy expressed in terms of its natural variables

We can use the combination of the first and second laws to derive an expression for the internal energy in terms of its natural variables. If we consider a reversible process:

$dU = \delta q + \delta w$
$\delta w = -PdV$ (definition of work)
$\delta q = TdS$ (second law rearranged)
Therefore, $dU = TdS - PdV$

This expression expresses the fact that the internal energy U has a T when the entropy changes and a slope -P when the volume changes. We will use this expression to derive the P and T dependence of the free energy functions.

The Gibbs energy expressed in terms of its natural variables

To find the natural variables for the Gibbs energy we begin with the internal energy:

$dU = TdS - PdV$

and substitute into:

$dH = dU + PdV + VdP$

to find:

$dH = TdS + VdP$ (S and P are natural variables of enthalpy)

and using:

$dG = dH - TdS - SdT$

we find:

$dG = -SdT + VdP$ (T and P are natural variables of G)

Once again we see why G is so useful. Its natural variables are ones that we commonly experience: T and P.