Gibbs Free Energy

We introduced the concept of the Helmholtz free energy to meet the conditions that a system be in a state with minimum energy and maximum potential. It describes systems at constant volume and temperature. We now want to introduce another free energy, the **Gibbs free energy**. This describes systems that are in equilibrium with constant pressure and temperature. The Gibbs free energy is defined to be

$$G = U - \tau\sigma + pV \tag{15.1}$$

Chemists often call this the free energy, while physicists often call it the thermodynamic potential. The most important property of the Gibbs free energy is that it is a minimum for a system in equilibrium at constant pressure when in thermal contact with a reservoir. In order to see this, consider the differential dG,

$$dG = dU - \tau d\sigma - \sigma d\tau + pdV + Vdp \tag{15.2}$$

If the system, S, is in thermal contact with a heat reservoir, R_1, at temperature τ and in mechanical contact with a pressure reservoir, R_2, that can maintain the pressure p but cannot exchange heat, then $d\tau = dp = 0$. So dG becomes

$$dG = dU - \tau d\sigma + pdV \tag{15.3}$$

From the thermodynamic identity

$$\tau d\sigma = dU - \mu dN + pdV$$

we see that

$$dG = \mu dN$$

but $dN = 0$, so $dG = 0$, which is the condition of an extremum. The fact that G is a minimum follows directly from the fact that the entropy has a minus sign associated with it. Also, from the derivation, we see that $G = G(\tau,p,N)$. The general differential of the Gibbs free energy is

$$dG = \left(\frac{\partial G}{\partial \tau}\right)_{N,p} d\tau + \left(\frac{\partial G}{\partial p}\right)_{\tau,N} dp + \left(\frac{\partial G}{\partial N}\right)_{p,\tau} dN$$

Comparing this with (15.2) and using the thermodynamic identity, we can immediately see that

$$\left(\frac{\partial G}{\partial N}\right)_{\tau,p} = \mu \tag{15.4}$$

$$\left(\frac{\partial G}{\partial \tau}\right)_{N,p} = -\sigma \qquad (15.5)$$

$$\left(\frac{\partial G}{\partial p}\right)_{N,\tau} = V \qquad (15.6)$$

Intensive and Extensive Quantities

The variables τ and p are called **intensive quantities**; they do not change value when two identical systems are put together. The variables U, σ, V, N and G are called **extensive quantities**; their values change when two identical systems are put together. For example, G depends on the number of particles, N. When two systems are brought together, then the number of particles for the combined system doubles, so the Gibbs free energy also doubles. Since the Gibbs free energy depends linearly on the number of particles, we can write

$$G = N\, \varphi(p,\tau)$$

Thus we see that

$$\left(\frac{\partial G}{\partial N}\right)_{p,\tau} = \varphi(p,\tau)$$

But we already saw that $\partial G/\partial N = \mu$, so $\varphi(p,\tau) = \mu$, and we get

$$G = N\,\mu(p,\tau) \qquad (15.7)$$

Thus, the chemical potential for a system is equal to the Gibbs free energy per particle. If more than one particle species is present, (15.7) becomes

$$G = \sum_j N_j \mu_j (p,\tau) \qquad (15.8)$$

With this change in definition, the differential dG becomes

$$dG = \sum_j \mu_j dN_j - \sigma d\tau + V dp \qquad (15.9)$$

Gibbs Free Energy and Helmholtz Free Energy

What is the difference between the Gibbs free energy and the Helmholtz free energy? Consider an ideal gas. We have already seen that the chemical potential for an ideal gas as a function of N, τ and V is given by

$$\mu(N,\tau,V) = \tau \ln \frac{N}{V n_q}$$

From the definition of the Helmholtz free energy we know that

$$\left(\frac{\partial F}{\partial N} \right)_{\tau,V} = \mu(N,\tau,V)$$

Holding τ and V constant and integrating, we get

$$F(N,\tau,V) = N\tau \left(\ln \frac{N}{V n_q} - 1 \right)$$

Thus, F is not directly proportional to N if we keep the temperature and volume constant. From the definition of the Gibbs free energy and the definition of the Helmholtz free energy we can immediately see that

$$G(N,\tau,p) = F + pV$$

$$= N\tau \left(\ln \frac{N}{V n_q} - 1 \right) + pV$$

$$= N\tau \left(\ln \frac{N}{V n_q} - 1 \right) + N\tau$$

since $pV = N\tau$ for an ideal gas. Thus

$$G(N,\tau,p) = N\tau \ln \frac{p}{\tau n_q} \tag{15.10}$$

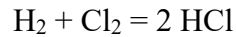From this we see that the chemical potential as a function of τ and p is

$$\mu(\tau,p) = \tau \ln \frac{p}{\tau n_q} \tag{15.11}$$

Chemical Reactions

How do we use the Gibbs free energy in a chemical reaction? We can write a chemical reaction as

$$\sum_j \nu_j A_j = 0 \qquad\qquad (15.12)$$

where A_j is the jth chemical species, and ν_j is the coefficient of the jth species in the reaction. For example, in the reaction

$$H_2 + Cl_2 = 2\ HCl$$

we have $A_1 = H_2$, $A_2 = Cl_2$, $A_3 = HCl$, $\nu_1 = 1$, $\nu_2 = 1$ and $\nu_3 = -2$. We usually discuss chemical equilibrium for reactions that occur under conditions of constant pressure and temperature. Recalling that the change in the Gibbs free energy is

$$dG = \sum_j \mu_j dN_j - \sigma d\tau + V dp$$

this reduces to

$$dG = \sum_j \mu_j dN_j$$

The change dN_j is proportional to the coefficient ν_j. This allows us to write

$$dN_j = \nu_j\, dx$$

where dx indicates how many times the reaction takes place. Thus dG becomes

$$dG = \sum_j \mu_j \nu_j dx$$

But in equilibrium $dG = 0$, so thus reduces to the condition

$$\sum_j \mu_j \nu_j = 0 \qquad\qquad (15.13)$$

Equilibrium Reactions in an Ideal Gas

If we treat each of the molecules as an ideal gas, we can cast this into a more familiar form. Recall that the chemical potential of an ideal gas is

$$\mu_j = \tau(\ln n_j - \ln c_j)$$

where $c_j = n_{q,j} Z_{\text{int},j}$. Substituting this into the equilibrium condition, we get

$$\sum_j \nu_j \ln n_j = \sum_j \nu_j \ln c_j$$

This can be rewritten as

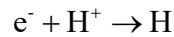$$\sum_j \ln n_j^{\nu_j} = \sum_j \ln c_j^{\nu_j}$$

or

$$\ln \prod_j n_j^{\nu_j} = \ln K(\tau) \qquad (15.14)$$

where $K(\tau) = \prod n_{q,j}^{\nu_j} e^{-\frac{\nu_j F_{\text{int},j}}{\tau}}$ is called the **equilibrium constant**. Exponentiating both sides of (15.14), we get the **law of mass action**,

$$\prod_j n_j^{\nu_j} = K(\tau) \qquad (15.15)$$

Example:
    Consider the reaction

$$e^- + H^+ \to H$$

The law of mass action yields

$$\frac{[e^-][H^+]}{[H]} = K(\tau)$$

$$= \frac{n_q(e^-) n_q(H^+)}{n_q(H)} e^{-\frac{I}{\tau}}$$

where $F_H(\text{int}) = -I = -13.6$ eV and I is the **ionization potential**. Here [A] is the concentration of the molecule A. The quantum concentration for H and H + is the same, $n_q(H) = n_q(H^+)$, so the mass action equation reduces to

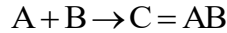$$\frac{[e^-][H^+]}{[H]} = n_q(e^-) e^{-\frac{I}{\tau}}$$

If charge neutrality is preserved, $[e^-] = [H^+]$, so this finally becomes

$$\left[e^-\right]=\left[H\right]^{\frac{1}{2}} n_q^{\frac{1}{2}} \left(e^-\right) e^{-\frac{I}{2\tau}}$$ (15.16)

This is called the **Saha equation.**

Reaction Speed

The law of mass action expresses the condition satisfied by the concentrations once the reaction has gone to equilibrium, but it tells nothing about how fast the reaction proceeds. Consider the reaction
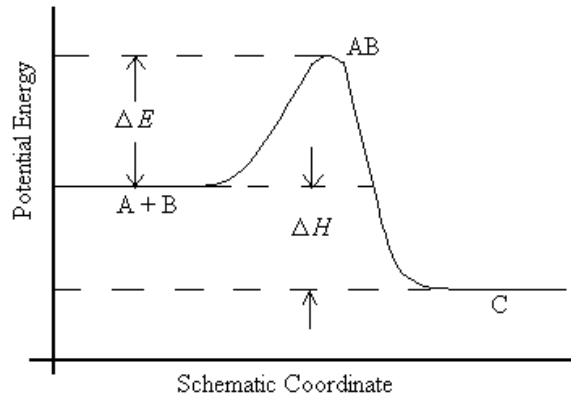
$$A + B \rightarrow C = AB$$

with concentrations n_A, n_B and $n_C = n_{AB}$. What is dn_{AB}/dt? We can write

$$\frac{dn_{AB}}{dt} = C(\tau) n_A n_B - D(\tau) n_{AB}$$

where $C(\tau)$ and $D(\tau)$ are constant with respect to rate. In equilibrium, $dn_{AB}/dt = 0$, so

$$\frac{n_A n_B}{n_{AB}} = \frac{D(\tau)}{C(\tau)}$$
$$= K(\tau)$$

In general, a graph of the potential energy required for a reaction looks like


Here ΔE is called the **activation energy**. This is the potential energy required for the reaction to take place. ΔH is called the **heat of reaction** and is the energy that evolves out of the reaction.

Isotherms

One of the uses of the Gibbs free energy is to plot the curve of pressure verses volume for a quantity of matter at constant temperature. This curve is called an **isotherm.**
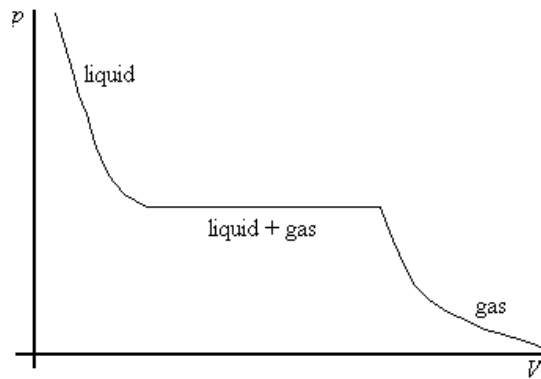
Different regions of the isotherm correspond to different forms of the matter, e.g. solid, liquid, or gaseous. The phase is a portion of a system that is uniform in composition. Two phases may coexist, with a definite boundary between them. Liquid and vapor (a gas that is in equilibrium with its liquid or solid form) may coexist on a section of an isotherm only if the temperature of the isotherm lies below a critical temperature, τ_c. Above that critical temperature only a single phase - the fluid phase - exists, no matter how great the pressure. Consider a system that is originally only a liquid at a constant temperature.
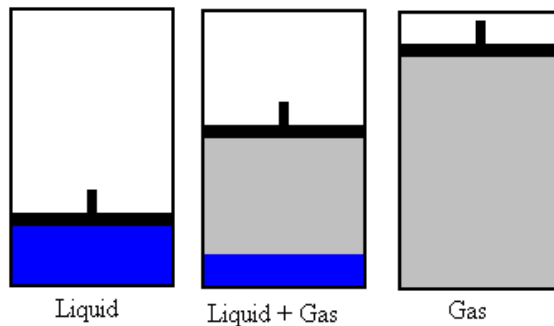
Raise the piston. As the piston is raised, more vapor is formed until there is only vapor in the chamber. Plotting the pressure verses volume for this transformation we get
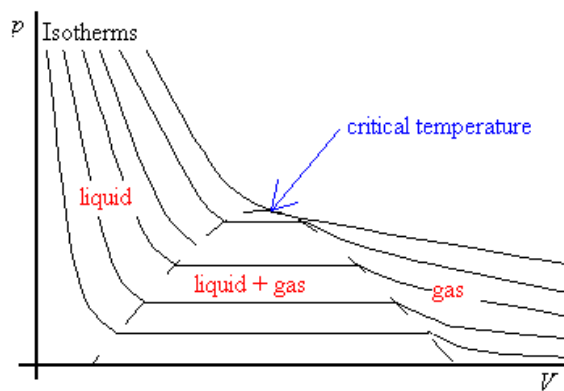
The thermodynamic conditions for the coexistence of two phases are the conditions for the equilibrium of two systems that are in thermal, diffusive and mechanical contact. These conditions are that

$$\tau_1 = \tau_2, \quad \mu_1(p,\tau) = \mu_2(p,\tau), \quad p_1 = p_2 \tag{15.17}$$

At a general point in the p-τ plane the two phases do not coexist: if $\mu_1 < \mu_2$, the first phase alone is stable, and if $\mu_1 > \mu_2$ the second phase alone is stable.

We see that $\mu_l(p,\tau) = \mu_g(p,\tau)$, so there must exist some form of **coexistence curve**. This is the curve that divides the phases on a $p\tau$ diagram.
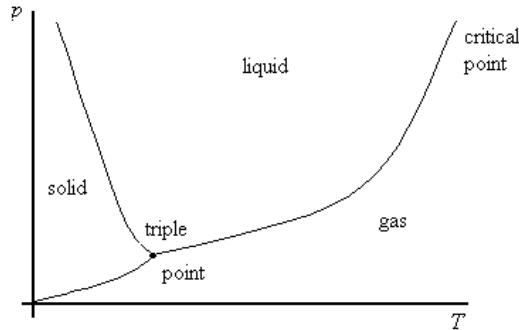
Consider a small segment of the curve. Then the condition for coexistence is that

$$\mu_l(p_0, \tau_0) = \mu_g(p_0, \tau_0) \tag{15.18}$$

and

$$\mu_l(p_0 + dp, \tau_0 + d\tau) = \mu_g(p_0 + dp, \tau_0 + d\tau)$$

Since the changes are small, we can expand the second condition to get

$$\mu_l(p_0, \tau_0) + \left(\frac{\partial \mu_l}{\partial p}\right)_\tau dp + \left(\frac{\partial \mu_l}{\partial \tau}\right)_p d\tau = \mu_g(p_0, \tau_0) + \left(\frac{\partial \mu_g}{\partial p}\right)_\tau dp + \left(\frac{\partial \mu_g}{\partial \tau}\right)_p d\tau \tag{15.19}$$

Subtracting (15.18) from (15.19) and rearranging the terms,

$$\frac{dp}{d\tau} = \frac{\left(\frac{\partial \mu_l}{\partial \tau}\right)_p - \left(\frac{\partial \mu_g}{\partial \tau}\right)_p}{\left(\frac{\partial \mu_l}{\partial p}\right)_\tau - \left(\frac{\partial \mu_g}{\partial p}\right)_\tau} \tag{15.20}$$

Now recall that the Gibbs free energy could be written as

$$G = N\mu(p,\tau) \Rightarrow \left(\frac{\partial G}{\partial p}\right)_{N,\tau} = V, \quad \left(\frac{\partial G}{\partial \tau}\right)_{N,p} = -\sigma$$

If we define the volume and entropy per molecule as $v = V/N$ and $s = \sigma/N$ respectively, then

$$\frac{\partial \mu}{\partial \tau} = \frac{\frac{\partial G}{\partial \tau}}{N}$$

$$= -\frac{\sigma}{N}$$

$$= s$$

and

$$\frac{\partial \mu}{\partial p} = \frac{\frac{\partial G}{\partial p}}{N}$$

$$= \frac{V}{N}$$

$$= v$$

so (15.20) becomes

$$\frac{dp}{d\tau} = \frac{s_g - s_l}{v_g - v_l} \tag{15.21}$$

Note that this derivative refers to the very special interdependent change of p and τ in which the gas and liquid continue to coexist. The number of molecules in each phase will vary as the volume is varied, subject only to the condition that $N_l + N_g = N$.

Enthalpy

Recall that the quantity of heat added to a system was related to the entropy by

$$dQ = \tau d\sigma$$

Thus the quantity of heat added by the transfer of one molecule is

$$dQ = \tau \left(s_g - s_l \right)$$
$$\equiv L \tag{15.22}$$

where L is called the **latent heat of vaporization**. If we write $v_g - v_l = \Delta v$, then (15.21) can be rewritten as

$$\frac{dp}{d\tau} = \frac{L}{\tau \Delta v} \tag{15.23}$$

This is known as the **Clausius-Clapeyron equation,** or the **vapor pressure equation**. Finally, the latent heat of a phase transition is, as we have seen, equal to τ times the entropy difference of the two phases at constant pressure. It is also equal to the difference in the **enthalpy**, H, of the two phases, where $H = U + pV$. To see this, consider the differential

$$dH = dU + pdV + Vdp$$
$$= \tau d\sigma + \mu dN + Vdp$$

by the thermodynamic identity. But at constant pressure this becomes

$$dH = \tau d\sigma + \mu dN$$

Considering the change across the coexistence curve, we see that the last term in dH becomes $(\mu_g - \mu_l)\Delta N$, while $dH \to \Delta H$ and $d\sigma \to \Delta\sigma$. But $\mu_g = \mu_l$ on the curve, so

$$\Delta H = \tau\Delta\sigma$$
$$= L$$

(15.24)

Using the definition of the heat capacity at constant pressure, this can be written in a more useful form. The heat capacity at constant pressure is given by

$$C_p = \tau \left(\frac{\partial\sigma}{\partial\tau} \right)_p$$
$$= \left(\frac{\partial U}{\partial\tau} \right)_p + p\left(\frac{\partial V}{\partial\tau} \right)_p$$
$$= \left(\frac{\partial H}{\partial\tau} \right)_p$$

Integrating this yields

$$H = \int C_p d\tau$$

(15.25)