Gibbs Energy; Thermodynamic Potential

The Gibbs energy of a system, \( G = U + p \cdot V - T \cdot S \) (a)

For a closed single phase system, changes in thermodynamic energy \( dU \) and Gibbs energy \( dG \) are related by the following equation.

\[
dG = dU + p \cdot dV + V \cdot dp - T \cdot dS - S \cdot dT \quad \text{(b)}
\]

The change in thermodynamic energy \( dU \) is related to the affinity for spontaneous change using the Master Equation.

\[
dU = T \cdot dS - p \cdot dV - A \cdot d\xi; \quad A \cdot d\xi \geq 0 \quad \text{(c)}
\]

We use equation (b) by substituting for \( dU \) in equation (a).

Hence, \( dG = -S \cdot dT + V \cdot dp - A \cdot d\xi; \quad A \cdot d\xi \geq 0 \) (d)

Chemists carry out most of their experiments under the twin conditions, constant pressure (usually ambient) and constant temperature (often near room temperature). Hence we can see why the latter equation is so important. At fixed \( T \) and \( p \),

\[
dG = -A \cdot d\xi; \quad A \cdot d\xi \geq 0 \quad \text{(e)}
\]

Hence under common laboratory conditions the direction of spontaneous change (e.g. chemical reaction) is in the direction for which \( G \) decreases. The spontaneous ‘flow’ of a chemical reaction (at fixed \( T \) and \( p \)) is down the plot of \( G \) against extent of reaction, \( \xi \); high to low \( G \). This statement opens the door to the quantitative study of chemical reactions. Thus from equation (e),

\[
A = -\left( \frac{\partial G}{\partial \xi} \right)_{T,p} \quad \text{(f)}
\]

The Gibbs energy decreases until the affinity for spontaneous change is zero; i.e. equilibrium.

\[
\text{Then, } \left( \frac{\partial G}{\partial \xi} \right)_{T,p}^{\text{eq}} = 0 \quad \text{(g)}
\]

At equilibrium the Gibbs energy is a minimum [1]. In general terms, a thermodynamic potential is an extensive property of a closed system which reaches an extremum at equilibrium under specified conditions. For processes in closed systems at fixed \( T \) and \( p \), the thermodynamic potential is \( G \). Thus \( T \) and \( p \) are the natural variables for \( G \).
Experience shows that for a given system there is one unique composition which corresponds to the minimum in Gibbs energy (at fixed T and p). In fact chemistry would be a very difficult subject (and it is difficult as it is) if there were many minima such that it was just a matter of chance which minimum a system ended up in following spontaneous chemical reaction.

The conclusions advanced above refer to the Gibbs energy of a closed system; i.e. a macroscopic property. We cannot at this stage draw conclusions about the properties of the chemical substances making up the system. At the molecular level a whole range of processes may be taking place; chemical reaction, diffusion, molecular collisions. We cannot comment on these using equation (g). It may be that one or more of these processes contributes towards an increase in Gibbs energy. However these processes operate in such a way that the fluctuations in Gibbs energies in small domains are opposed, holding the overall system at a minimum in G.

The Gibbs energy is a contrived property. It is not the ‘energy’ of the system. Nevertheless we can begin to ‘understand’ this property by returning to equation (d). Consider a system at equilibrium and at constant temperature; i.e. $A = 0$ and $dT = 0$.

Then 

$$V = \left( \frac{\partial G}{\partial p} \right)_{T,A=0} \quad (h)$$

The familiar property, volume, is the differential dependence of Gibbs energy on pressure at constant temperature and at equilibrium. If we can assume that the coffee mug on this desk is at equilibrium, although I do not know (and can never know) its Gibbs energy, I know that the volume offers a direct measure of the dependence of its Gibbs energy on pressure. Indeed the link between a property which can be readily measured (e.g. volume or density) offers chemists a pathway into the Gibbs energy and a detailed thermodynamic analysis.

**Footnote**