Helmholtz Energy

Gibbs energy is defined with practical chemistry in mind because the definition centres on closed systems held at constant temperature and constant pressure. A similar interest prompt definition of the Helmholtz energy, symbol $F$.

By definition, \[ F = U - T \cdot S \] (a)

Physicists use the term ‘Helmholtz Function’. The old term ‘Helmholtz free energy’ is not encouraged [1]. If a closed system is displaced to a neighboring state, the differential change in Helmholtz energy is given by equation (b).

\[ dF = dU - T \cdot dS - S \cdot dT \] (b)

But the differential change in thermodynamic energy is given by the Master Equation. By incorporating the latter into equation (b), we obtain equation (c), the memorable “all-minus” equation.

\[
\begin{align*}
\frac{dF}{dA} = -S \cdot dT - p \cdot dV - A \cdot d\xi \\
A \cdot d\xi \geq 0
\end{align*}
\] (c)

At fixed temperature and fixed volume (isothermal and isochoric conditions),

\[ dF = -A \cdot d\xi \] (d)

All spontaneous processes at fixed temperature and fixed volume lower the Helmholtz energy of a closed system. In practical terms, for a closed system held at constant volume and temperature, chemical reaction (molecular reorganization) lowers the Helmholtz energy of the system [2]. We presume that the pressure inside the reaction vessel will change, decreasing for some systems and increasing for other systems. As it stands thermodynamics offers no generalization concerning how the pressure changes. In fact if we want to use the Helmholtz energy as an indicator of the direction of spontaneous change we would build the reaction vessel with thick steel walls. This is a practical possibility and so the Helmholtz energy is a practical thermodynamic potential.

For equilibrium transformations (i.e. at constant $A = 0$),

\[
S = -\left(\frac{\partial F}{\partial T}\right)_{V,A=0} \] (e)
Similarly [3] $p = -\left(\frac{\partial F}{\partial V}\right)_{T,A=0}$  

**Footnotes**

[1] Since the product $T \cdot S$ is the linked energy, equation (a) shows that $F$ is the ‘free energy’ of the system.


(a) Liquid transport;  

(b) Ionic Conductances in Solution.  

(c) Chemical kinetics

(d) Chemical Equilibria.  


Thus $S = -\left(\frac{\partial F}{\partial T}\right)_{V,\xi}$ and, $p = -\left(\frac{\partial F}{\partial V}\right)_{T,\xi}$