

Properties of thermodynamic functions

We established that under constant pressure P_0 and temperature T_0

$$\delta W \leq -\delta \Phi$$

Consider a process in which the system does not do any work

$$\delta \Phi \leq 0$$

$$\delta (E - T_0 S + P_0 V) \leq 0$$

"=" corresponds to reversible processes and "<" is for irreversible processes. So, Φ never increases. In the case of an isolated system $\delta E \geq 0, \delta V \geq 0$, so

$$\delta S \geq 0$$

In an isochoric isothermal process

$$\delta F = \delta (E - T_0 S) = \delta F \leq 0$$

In some sense, the free energy here is equivalent to entropy; it may serve as a criterion of irreversibility of a process

Example: when you dissolve sugar in water or any substance in a liquid, without any change of volume, the free energy decreases

Note: in experiment isobaric processes are

Note: in experiment isobaric processes are more common

$$F = E - TS$$

$$dF = dE - TdS - SdT = -PdV - SdT$$

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$$P = -\left(\frac{\partial F}{\partial V}\right)_T$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_V$$

$$\Phi = E - TS + PV$$

$$d\Phi = dE - TdS - SdT + PdV + VdP = -SdT + VdP$$

$$V = -\left(\frac{\partial \Phi}{\partial P}\right)_T$$

$$S = -\left(\frac{\partial \Phi}{\partial T}\right)_P$$

There are other useful inequalities:

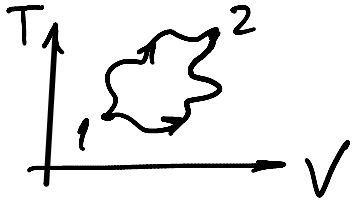
$$\left(\frac{\partial P}{\partial T}\right)_V = -\frac{\partial^2 F}{\partial V \partial T} = \left(\frac{\partial S}{\partial V}\right)_T$$

$$\left(\frac{\partial V}{\partial T}\right)_S = -\frac{\partial^2 \Phi}{\partial P \partial T} = -\left(\frac{\partial S}{\partial P}\right)_T$$

← Maxwell relations

Usually it's enough to describe a system by

Usually it's enough to describe a system by a pair of macroscopic parameters. For instance, if it is V and T , then F plays the role of an important function, which is a function of these parameters



If P and T are the variables, then Φ is the proper function to be looked at. $\Phi = \Phi(P, T)$

what about enthalpy?

$$H = E + PV$$

$$dH = dE + PdV + VdP = TdS + VdP$$

$$H = H(S, P)$$

$$\begin{array}{l} T = \left(\frac{\partial H}{\partial S} \right)_P \\ V = \left(\frac{\partial H}{\partial P} \right)_S \end{array}$$

$$\left(\frac{\partial T}{\partial P} \right)_S = \frac{\partial^2 H}{\partial S \partial P} = \left(\frac{\partial V}{\partial S} \right)_P$$

another Maxwell relation

Note: the above thermodynamic functions are also not independent:

$$F = F + TS = F - T \left(\frac{\partial F}{\partial T} \right)_V \quad \left. \vphantom{F = F + TS} \right\} \text{Gibbs-Helmholtz}$$

also note that

$$E = F + TS = F - T \left(\frac{\partial F}{\partial T} \right)_V$$

$$H = \varphi - TS = \varphi - T \left(\frac{\partial \varphi}{\partial T} \right)_P$$

Gibbs-Helmholtz
relations