

Chapter 5 - Free energy and chemical thermodynamics

Some thermodynamic variables will increase when you increase the amount of stuff. Such variables are called **extensive**, and include V, m, N, S, U, H, F and G . **Intensive** variables will *not* increase, and include T, P, ρ and μ .

- extensive \times intensive = extensive
- $\frac{\text{extensive}}{\text{intensive}} = \text{intensive}$
- extensive + extensive = extensive etc

Free energies

We call them free energies because they represent the energy one would be free to use after annihilating the system.

Enthalpy is the total energy one would need to create a system out of nothing, and place it in an environment with constant pressure.

$$H = U + PV$$

Differentiating and using $dU = TdS - PdV + \mu dN$ gives its thermodynamic identity:

$$dH = \left(\frac{\partial H}{\partial S}\right)_{N,P} dS + \left(\frac{\partial H}{\partial P}\right)_{N,S} dP + \left(\frac{\partial H}{\partial N}\right)_{S,P} dN = TdS + VdP + \mu dN$$

Constant NVT - Canonical ensemble

Helmholtz' free energy is the energy required to create a system, minus the heat freely available from the temperature of its environment.

$$F = U - TS$$

It also has a thermodynamic identity:

$$dF = \left(\frac{\partial F}{\partial V}\right)_{N,T} dV + \left(\frac{\partial F}{\partial T}\right)_{N,V} dT + \left(\frac{\partial F}{\partial N}\right)_{T,V} dN = -PdV - SdT + \mu dN$$

In general one will find that $\Delta F \leq W$ at constant temperature.



We can reformulate the second law for this ensemble: $\Delta F \leq 0$

Constant NPT

Gibbs' free energy is the work that must be done to create a system in an environment with constant pressure and temperature.

$$G = U + PV - TS = H - TS$$

It is vital in chemistry, where $\Delta G \leq 0$ means that a process will happen spontaneously.

$$\Delta G = \Delta H - T\Delta S$$



Once again we find another formulation of the second law: $\Delta G \leq 0$

As always, there is a thermodynamic identity.

$$dG = \left(\frac{\partial G}{\partial P} \right)_{N,T} dP + \left(\frac{\partial G}{\partial T} \right)_{N,P} dT + \left(\frac{\partial G}{\partial N} \right)_{P,T} dN = VdP - SdT + \mu dN$$

The chemical potential μ gives the amount of Gibbs energy per particle, aka $G = N\mu$. This means that the Gibbs energy of a system can be used to find its chemical potential.

$$\frac{\partial}{\partial P} \mu = \frac{\partial}{\partial P} \frac{G}{N} \Rightarrow \frac{\partial \mu}{\partial P} = \frac{V}{N} = \frac{kT}{P} \Rightarrow \mu(T, P) - \mu(T, P^0) = kT \ln(P/P_0) \Rightarrow \mu(T, P) = \mu(T, P^0) + kT \ln(P/P^0)$$

Constant μVT - Grand canonical ensemble

The **Grand potential** describes irreversible processes in open systems.

$$\Phi = U - TS - \mu N$$

It has a fun identity, how surprising.

$$d\Phi = \left(\frac{\partial \Phi}{\partial V} \right)_{\mu,T} dV + \left(\frac{\partial \Phi}{\partial T} \right)_{\mu,V} dT + \left(\frac{\partial \Phi}{\partial \mu} \right)_{V,T} d\mu = -PdV - SdT - Nd\mu$$

Maxwell relations

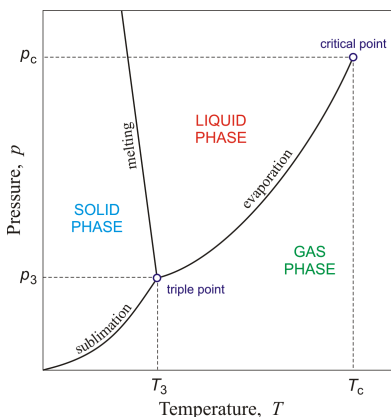
Thermodynamic potentials have a symmetry of their second derivatives with respect to their natural variables. For ex $\frac{\partial^2 U}{\partial V \partial S} = \frac{\partial^2 U}{\partial S \partial V}$. N is *not* a natural variable! So we have $U(S, V)$, $H(S, P)$, $F(V, T)$ and $G(P, T)$. Notice that the state variables in parentheses come from each thermodynamic identity, minus N .

Phase transformations

A discontinuous change in the properties of a substance when its environment changes infinitesimally is called a **phase transformation**.

Pure substances

The **phase diagram** of a pure substance shows the equilibrium states as a function of pressure and temperature. At the **vapour pressure** it is possible for the gas phase to coexist with liquid and solid. The **triple point** is a temperature and pressure where all three phases may coexist simultaneously. Past the **critical point** one can no longer discern gas from liquid, and will simply have to refer to the whole mess as a **fluid**.



! The stable phase of a substance at given conditions is always the one with the lowest Gibbs energy.

One can find the pressure dependence of the Gibbs energy by using $(\partial G/\partial P)_{T,N} = V$. Similarly for temperature one can use $(\partial G/\partial T)_{P,N} = -S$. These two relations can be used to find the slope of the boundary between gas and liquid on the phase diagram, as $G_g = G_l$ at this boundary:

$$\frac{dP}{dT} = \frac{S_g - S_l}{V_g - V_l} = \frac{H_g - H_l}{T(V_g - V_l)}$$

Setting $S_g - S_l = L/T$ gives the **Clausius-Clapeyron-relation** $\frac{dP}{dT} = \frac{L}{T\Delta T}$, which applies to any phase boundary line on a PT -diagram.

One can model a gas-liquid system with **Van der Waals equation**, which is an improved equation of state based on the ideal gas.

$$\left(P + \frac{aN^2}{V^2}\right)(V - Nb) = NkT$$

The constant b is the smallest possible volume occupied by a molecule when in contact with its neighbours, while the term aN^2/V^2 describes the attractive forces between molecules who are close but not touching.