

Review of classical thermodynamics

Fundamental Laws, Properties and Processes (3)

Fundamental equations

The Helmholtz Free Energy

The Gibbs Free energy

Changes in composition

Chemical potential

Thermodynamic relations

Reading: Chapter 5.1 – 5.9 of Gaskell
or the same material in any other textbook on thermodynamics

Fundamental equations

Combined statement of 1st and 2nd Laws of Thermodynamics:

$$dU = TdS - PdV$$

This equation gives us

- Relationship between the dependent variable U and independent variables V and S : $U = U(S,V)$ or $dU = (\partial U/\partial S)_V dS + (\partial U/\partial V)_S dV$
- The criteria for equilibrium: in a system of constant V and S , the internal energy has its minimum value, or, in a system of constant U and V , the entropy has its maximum value.

The problem is that the pair of independent variables (V,S) is rather inconvenient – entropy is hard to measure or control. We want to have fundamental equations with independent variables that is easier to control. The two convenient choices are:

P and T pair – the best choice from the practical point of view, easy to control/measure. For systems with constant pressure the best suited state function is **the Gibbs free energy** (also called free enthalpy) $G = H - TS$

V and T pair – easy to examine in statistical mechanics. For systems with constant volume (and variable pressure), the best suited state function is **the Helmholtz free energy** $A = U - TS$

Any state function can be used to describe any system (at equilibrium, of course), but for a given system some are more convenient than others.

The Helmholtz Free Energy

$$A = U - TS \Rightarrow dA = dU - TdS - SdT$$

Combining this equation with $dU = TdS - PdV$ we get

$$dA = -PdV - SdT \quad \text{- fundamental equation}$$

$$A = A(T, V) \Rightarrow dA = (\partial A / \partial T)_V dT + (\partial A / \partial V)_T dV$$

Comparing the equations we see that

$$S = -(\partial A / \partial T)_V$$

$$P = -(\partial A / \partial V)_T$$

At constant T and V the equilibrium states corresponds to the minimum of Helmholtz Free Energy ($dA = 0$). From $A = U - TS$ we see that low values of A are obtained with low values of U and high values of S .

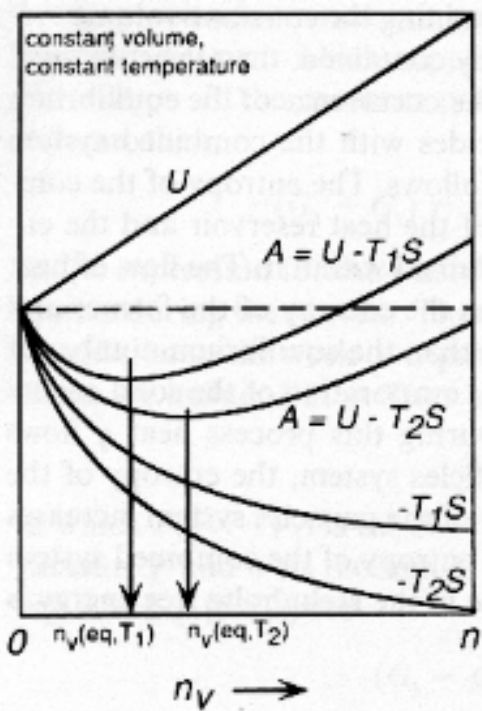


Illustration by Gaskell on the criterion for equilibrium in a closed solid-vapor system at constant V and T . The transfer of one atom to vapor increases U by a sublimation energy, whereas increase of entropy is slowing down with increasing number of atoms in the vapor phase, n_v .

The Gibbs Free Energy

$$G = H - TS = U + PV - TS \Rightarrow dG = dU + PdV + VdP - TdS - SdT$$

Combining this equation with $dU = TdS - PdV$ we get

$$dG = VdP - SdT \quad \text{- fundamental equation}$$

$$G = G(T, P) \Rightarrow dG = (\partial G / \partial P)_T dP + (\partial G / \partial T)_P dT$$

Comparing the equations we see that

$$S = - (\partial G / \partial T)_P$$
$$V = (\partial G / \partial P)_T$$

For an isothermal-isobaric system the equilibrium state corresponds to the minimum of the Gibbs Free Energy ($dG=0$). From $G=H-TS$ we see that low values of G are obtained with low values of H and high values of S .

Summary of the equations for a closed system

$$dU = \delta q - \delta w$$

$$dU = TdS - PdV$$

$$H = U + PV$$

$$dH = TdS + VdP$$

$$A = U - TS$$

$$dA = -PdV - SdT$$

$$G = H - TS$$

$$dG = VdP - SdT$$

Gibbs Free Energy: Equilibrium is Trade-off Between Enthalpy and Entropy

$$G = H - TS$$

A change to a lower enthalpy state ($\Delta H < 0$) usually decreases the randomness ($\Delta S < 0$):

- Freezing of a liquid
 - Oxidation of a metal
- | \Rightarrow exothermic processes

A change to a higher entropy state ($\Delta S > 0$) usually increases the enthalpy ($\Delta H > 0$)

- Melting of a solid
 - Evaporation of a liquid
 - Dissolution of salt in water
- | \Rightarrow endothermic processes

All of these processes are characterized by a lowering of the Gibbs free energy:

$$\Delta G = \Delta(H - TS) < 0$$

A crystal at equilibrium has its minimum Gibbs free energy:

$$G = H - TS = \text{minimum}$$

(if $T = \text{const}$ and $P = \text{const}$)

Variation of number of particles and composition

If the number of particles and/or composition of the system changes during a process, then two independent variables are not sufficient to describe the state of the system. Chemical reactions or exchange with surroundings can lead to the change in composition (number of moles of different species, n_i, n_j, n_k, \dots).

The Gibbs free energy (as well as other thermodynamic potentials) is an extensive property – depends on size of the system and on number of moles of different species, $G = G(T, P, n_i, n_j, n_k, \dots)$.

$$dG = \left(\frac{\partial G}{\partial P}\right)_{T, n_i, n_j, \dots} dP + \left(\frac{\partial G}{\partial T}\right)_{P, n_i, n_j, \dots} dT + \left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_j, n_k, \dots} dn_i + \left(\frac{\partial G}{\partial n_j}\right)_{T, P, n_i, n_k, \dots} dn_j + \text{etc.}$$

If composition is not changing, $dG = VdP - SdT$ and, therefore,

$$S = -(\partial G / \partial T)_{P, n_i, n_j, \dots} \quad \text{and} \quad V = (\partial G / \partial P)_{T, n_i, n_j, \dots}$$

$$\text{Therefore:} \quad dG = -SdT + VdP + \sum_{i=1}^{i=k} \left(\frac{\partial G}{\partial n_i}\right)_{P, T, n_i, \dots} dn_i$$

Where $\left(\frac{\partial G}{\partial n_i}\right)_{P, T, n_j, \dots} = \mu_i$ is chemical potential of the species i

$$dG = -SdT + VdP + \sum_{i=1}^{i=k} \mu_i dn_i$$

The Chemical Potential

The chemical potential of the species i is the rate of increase of G with n_i when species i are added/generated in the system at constant T , P , and number of moles of all the other species.

$$\left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_j,\dots} = \mu_i \quad dG = -SdT + VdP + \sum_{i=1}^k \mu_i dn_i$$

This equations can be applied to **open systems** that exchange both matter and heat with their surroundings, as well as to **closed systems** where changes in composition are due to chemical reactions.

Similar equations can be written for U , H , and A :

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_j,\dots} = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_j,\dots} = \left(\frac{\partial H}{\partial n_i}\right)_{S,P,n_j,\dots} = \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_j,\dots}$$

$$dU = TdS - PdV + \sum_{i=1}^k \mu_i dn_i \quad dH = TdS + VdP + \sum_{i=1}^k \mu_i dn_i$$

$$dA = -SdT - PdV + \sum_{i=1}^k \mu_i dn_i \quad dG = -SdT + VdP + \sum_{i=1}^k \mu_i dn_i$$

We can rewrite the 1st Law for a closed system undergoing a reversible change in composition due to a chemical reaction:

$$dU = \delta q - \delta w \quad \delta q = TdS \quad \delta w = PdV - \sum_{i=1}^k \mu_i dn_i$$

Where $-\sum_{i=1}^k \mu_i dn_i$ is the chemical work done by the system

Thermodynamic Relations

From the equations

$$dU = TdS - PdV + \sum_{i=1}^k \mu_i dn_i$$

$$dH = TdS + VdP + \sum_{i=1}^k \mu_i dn_i$$

$$dA = -SdT - PdV + \sum_{i=1}^k \mu_i dn_i$$

We can obtain the following thermodynamic relations:

$$dG = -SdT + VdP + \sum_{i=1}^k \mu_i dn_i$$

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{P,T,n_j,\dots} = \left(\frac{\partial U}{\partial n_i} \right)_{S,V,n_j,\dots} = \left(\frac{\partial H}{\partial n_i} \right)_{S,P,n_j,\dots} = \left(\frac{\partial A}{\partial n_i} \right)_{T,V,n_j,\dots}$$

$$T = \left(\frac{\partial U}{\partial S} \right)_{V,\text{comp}} = \left(\frac{\partial H}{\partial S} \right)_{P,\text{comp}}$$

$$P = - \left(\frac{\partial U}{\partial V} \right)_{S,\text{comp}} = - \left(\frac{\partial A}{\partial V} \right)_{T,\text{comp}}$$

$$V = \left(\frac{\partial H}{\partial P} \right)_{S,\text{comp}} = \left(\frac{\partial G}{\partial P} \right)_{T,\text{comp}}$$

$$S = - \left(\frac{\partial A}{\partial T} \right)_{V,\text{comp}} = - \left(\frac{\partial G}{\partial T} \right)_{P,\text{comp}}$$

Summary

Make sure you understand language and concepts:

- Fundamental equations
- The Helmholtz Free Energy
- The Gibbs Free energy
- Changes in composition
- Chemical potential
- Thermodynamic relations

A thermodynamic system consisting of many interacting particles and some externally fixed conditions (e.g. constant temperature), is in equilibrium if the best possible balance between a small energy and a large entropy is achieved.

Both quantities are typically opposed to each other: High entropies mean high energies and vice versa. The entropy part becomes more important at high temperatures.

Thermodynamic potential which has to be minimized for systems under constant pressure, is the Gibbs free energy, $G = H - TS$

If you have a system with constant volume (and variable pressure), the best suited state function is the Helmholtz free energy, $A = U - TS$