

CHEM 3410: Physical Chemistry I — Fall 2009

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Lecture 13: Gibbs Free Energy & Equilibrium

References

1. Brady, *Physical Chemistry*, Sections 4.1–4.5

Key Concepts

- Last time we developed a new function, the Gibbs Free Energy ($G(T, P)$), a new thermodynamic energy function that was minimized at equilibrium under constant pressure and temperature conditions.

$$G = U - TS + PV$$

- Using our definition of enthalpy ($H = U + PV$) we can write $G = H - TS$. If we look at small changes in G at constant temperature, this reduces to $dG = dH - TdS$. For macroscopic changes we can integrate this to give us an expression that looks very familiar:

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

- A similar derivation is possible under conditions of constant V and T , which yields the Helmholtz Free Energy ($A(V, T)$ in our book):

$$A = U - TS$$

$$dA = -TdS - PdV$$

- From these new functions, we can develop additional expressions by comparing the forms derived above with the expressions we used for a function that was an exact differential (state function):

$$dG = \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP$$

Comparing this with $dG = -SdT + VdP$ we arrive at the following:

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \text{ and } \left(\frac{\partial G}{\partial P}\right)_T = V$$

and the following Maxwell relations (the derivative of G with respect to first T and then P must be equal to taking the derivative of G with respect to P first and then T).

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

Experimental Conditions	Key Fundamental Parameter	At Equilibrium	Spontaneous Process	At Equilibrium
Isolated	S	maximized	$\Delta S > 0$	$dS = 0$
Constant T & P	G	minimized	$\Delta G < 0$	$dG = 0$
Constant T & V	A	minimized	$\Delta A < 0$	$dA = 0$

- We can apply the condition that the Gibbs Free energy is a minimum at equilibrium for systems at constant P and T to situations where other forms of work are important, such as where surfaces (or interfaces) are being created and destroyed.

$$dG = -SdT + VdP + \gamma dA$$

where A is the surface area and γ is the surface energy (the cost for having an interface between two substances). At constant T and P this reduces to:

$$dG = \sum \gamma_i dA_i$$

where is a sum over all the surfaces and respective surfaces energies in the system. At equilibrium, $dG = 0$ and we were able to develop the equilibrium conditions for spontaneous wetting of a surface by another material.

- Another type of work that will be very important is chemical work. This is an important consideration when the composition of a system can change, such as during a chemical reaction. In this case, G will be a function of T , P and the composition variables n_i , where n_i are the number of moles of species i .
- For a two component systems (species 1 and 2) we can write:

$$dG = \left(\frac{\partial G}{\partial T} \right)_{P, n_1, n_2} dT + \left(\frac{\partial G}{\partial P} \right)_{T, n_1, n_2} dP + \left(\frac{\partial G}{\partial n_1} \right)_{T, P, n_2} dn_1 + \left(\frac{\partial G}{\partial n_2} \right)_{T, P, n_1} dn_2$$

The last two terms in the above expression are *partial molar quantities*. They represent the change in free energy when the amount of one component is changed, holding all other constant. We define this quantity as the chemical potential:

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T, P, n_{j \neq i}}$$

- So in general, for a system of i components (compounds, elements, etc.) we can write dG as:

$$dG = -SdT + VdP + \sum_i \mu_i dn_i$$

which at constant temperature and pressure reduces to:

$$dG = \sum_i \mu_i dn_i$$