

CHEM 3410: Physical Chemistry I — Fall 2009

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Lecture 12: Equilibrium & Gibbs Free Energy

References

1. Levine, *Physical Chemistry*, Sections 4.1–4.4

Key Concepts

- We can now try to understand how to develop criteria for equilibrium in simple systems and then try to move onto more complex and real systems.
- We can apply the combined first and second law to an isolated systems to determine conditions for equilibrium. For this type of system, **entropy** is maximized at equilibrium.
- For thermal equilibrium between two isolated bodies at different temperatures, our physical intuition tells us that equilibrium is reached when the temperatures are equal. This can be shown formally by employing our expression of dU in terms of dS and dV and making some simplifications due to the isolated nature of the system. At equilibrium the entropy must be a maximum.
- A similar argument can be made, using the maximization of entropy, for an isolated system where the total volume is constrained but there is an internal partition that is moveable. In this case, the total internal energy and volume of the system are fixed, however both U and V can be different in different parts of this system. At equilibrium, we showed that the temperature and pressures must be uniform:

$$T_A = T_B \text{ and } P_A = P_B$$

This makes sense based on our physical intuition since the partition would move if the pressures were different on each side. If the temperatures were different, heat would flow from the higher temperature region to the lower temperature region.

- For most “real” world applications, systems are not isolated. Heat and work can flow across the boundaries of the system from the surroundings. This leads to two main problems:
 1. The internal energy of the system can now fluctuate.
 2. The system is now in contact with the surroundings and we need to consider the changes of entropy for the surroundings are well as for the system.
- In this case we need to find a function that describes our system of interest. We can do this by fixing the intensive variables T and P at the boundary (typical laboratory conditions are constant pressure and temperature). We can now find a thermodynamic function whose independent variables are those controlled at the boundaries. So in this case, we’d like a function that depends on T and P . This function would be minimized at equilibrium.
- The Gibbs Free Energy (G) describes a system under these conditions ($G(T, P)$) and can be written as:

$$G = U - TS - PV$$

$$dG = -SdT + VdP$$

We have taken out the thermal energy and compressive/mechanical energy from the internal energy in arriving at this function. This is useful because all of the other kinds of work (chemical, electrical, etc) are left. So at constant T and P :

$$dG = \partial w_{other}$$

which will be of great interest for us in considering system where chemical work is done (reactions, multi-phase systems), surface work (solid forming from a liquid), etc.