

September 2009

# Hierarchical Subject Inter-relations in Physical Chemistry

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## Recommended Citation

David, Carl W., "Hierarchical Subject Inter-relations in Physical Chemistry" (2009). *Chemistry Education Materials*. 86.  
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# Hierarchical Subject Inter-relations in Physical Chemistry

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## Abstract:

Students mystified by the progression of topics in Physical Chemistry may gain insight into their path through the material if acquainted with the diagrams presented and discussed herein. *The incredible delay in refereeing this manuscript, prompts me to release this preprint early (1/26/09).onsciousable*

## Introduction:

Studying Physical Chemistry can be a daunting task for students whose understanding of the placement of the subtopics keeps them mired in the details of individual aspects of the subject. Why do we study thermodynamics? Why do we study Quantum Mechanics? Why the Carnot engine? Why van der Waals gases?

I've found it helpful to show students two diagrams, one reading top to bottom which gives some perspective on how and why we're studying thermodynamics (Figure 1) and one (Figure 2) which reads from bottom to top indicating how the thermodynamics and quantum mechanics dovetail to give an understanding and appreciation of chemical equilibrium.

## Explanation of the Diagrams:

The standard Physical Chemistry curriculum starts with ideal (and non-ideal) gases, and progresses on to thermodynamics. The path is strewn with obstacles which seem incongruous in their difficulty, abstractness, and arbitrariness to many students, especially those who do not trust that there is method in the madness. To these latter students, each sub-topic is disconnected from previous topics, and has little or no relevance to any larger picture which is supposed to be emerging.

It is sometimes helpful to offer students at the outset a map of where they are going, and why. Especially for juniors in Physical Chemistry, who have done chemical equilibrium problems in Freshman Chemistry, the goal of explicating where the formulas they "memorized" and/or learned to use came from, is a worthwhile one. Showing them that, aside from their intrinsic interest, gases allow us to provide tractable examples for future work in thermodynamics may make the study of gases more palatable.

Periodic reference to this map as we passed from topic to topic allowed my students to understand where they were going, and why. When one gets, however, to gaseous equilibrium and attempts to make the transition of non-gaseous systems, the murkiness of the subject defies simple diagram construction, and so our map ends with fugacity, activity, etc.. Kinetics is not treated here, and neither is phase equilibrium.

In the second diagram, which commonly treats the theoretical aspects of Physical Chemistry discussed in the second semester, the motivation of quantum chemistry leading to statistical thermodynamics leading to an explanation of the origin of chemical equilibrium is stressed, leaving aspects of quantum chemistry, specifically structure, spectroscopy, etc., out of the diagram. This is not to diminish their importance, but to continue to stress the *raison-d'être* for the thermodynamics study, as well as explaining the identity problem in thermodynamics, i.e., that thermodynamics does not know the differences between substances except as they are

presented empirically through experimentally determined constants in various equations (heat capacity, compressibility,  $\Delta H_f^\circ$ , etc.).

### **Discussion:**

Since all the material included in these diagrams comes as second nature to persons who teach this material, it is important to understand how mysterious the whole process is to students whose struggle with the calculus precludes their gaining perspective on the actual material being considered. Typically, for example, an aside into calorimetry, with its myriad of problems which need to be solved in ascending order of difficulty, confuses the student when s/he considers the larger aspects of the course, hence the suggestion that these diagrams (or similar ones) be referenced at appropriate times to keep students aware of the overall path they are taking. Details and subtopics should not be allowed to obscure the overall goal. Some variant on this set of drawings may be helpful to others, so they are offered here.

Suggestions for improvements of the diagrams would be gratefully appreciated.

### **Figures:**

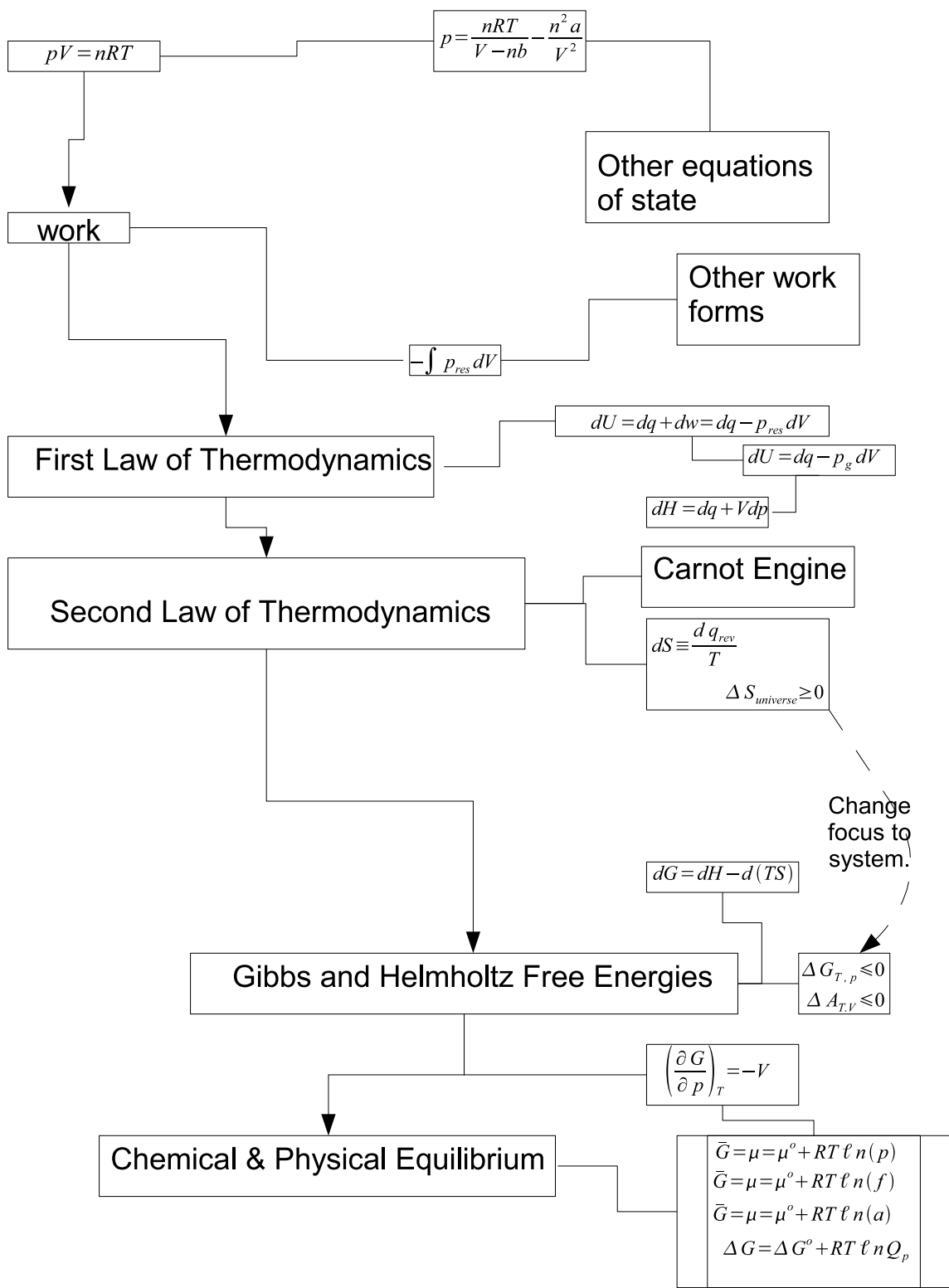


Figure 1: Chemical Equilibrium from Thermodynamics

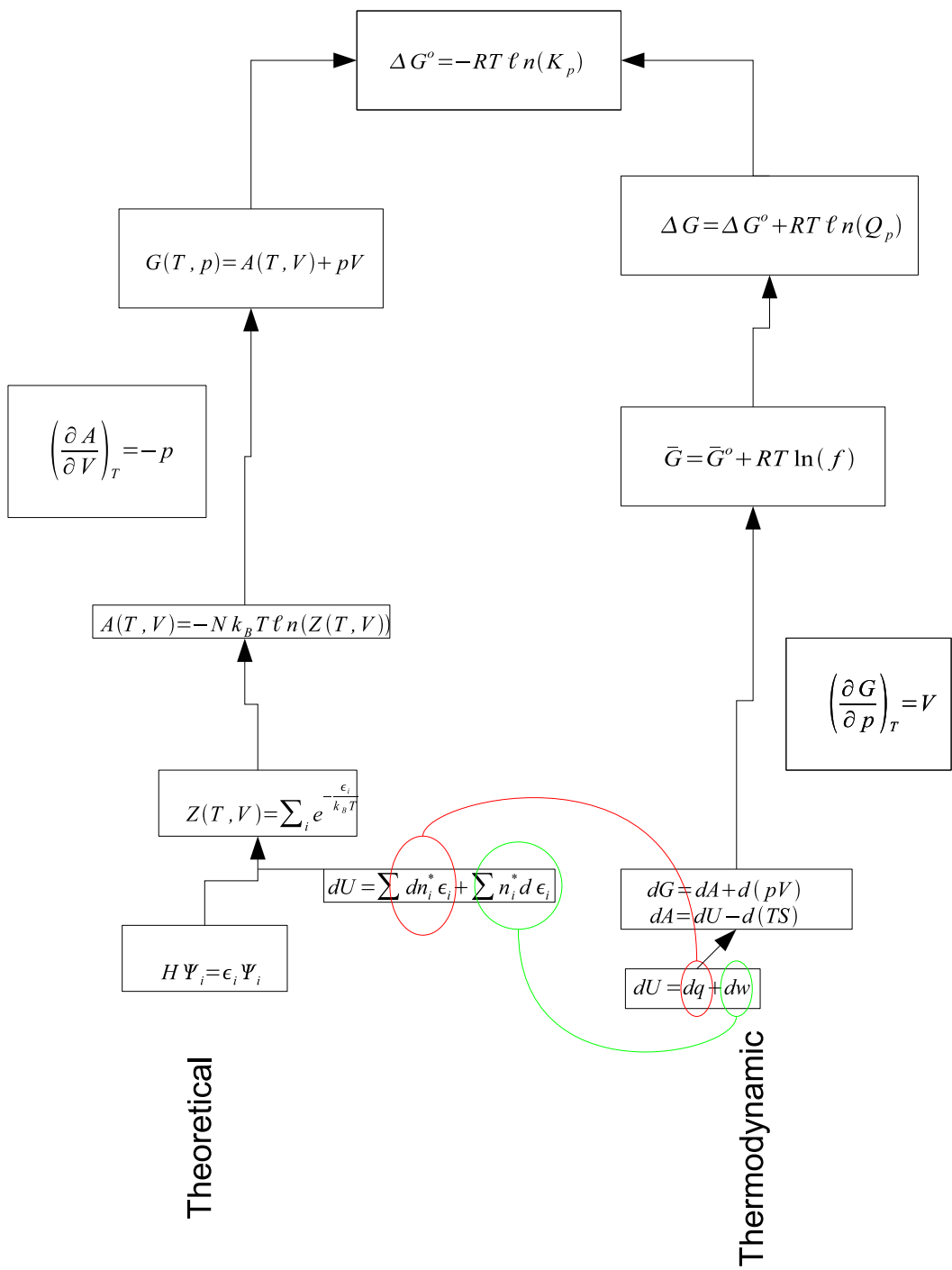


Figure 2: Chemical Equilibrium from Quantum and Statistical Thermodynamics