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# Rationale for Studying Physical Chemistry

Carl W. David

*University of Connecticut*, [Carl.David@uconn.edu](mailto:Carl.David@uconn.edu)

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# Rationale for Studying Theoretical Chemistry

C. W. David

*Department of Chemistry*

*University of Connecticut*

*Storrs, Connecticut 06269-3060*

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## I. SYNOPSIS

The various rationales for studying physical chemistry, and specifically the theoretical component thereof are presented in what is hoped in a coherent package.

## II. WHY STUDY P. CHEM.

After one's finished a year of physical chemistry, one has the right to ask what have I learned, and why was I forced to learn it?

And the answer is ...

### A. First Justification

Actually, the answer is far from clear. At one level, learning physical chemistry is learning how to “plug-and-chug” using equations (either learned or looked up), keeping units straight, etc.. The argument justifying this process is that applying the right equation (previously known) to the right physical situation is, *a priori*, of value. After all, the majority of chemists will only use equations derived by others, if at all.

### B. Second Justification

At a slightly higher level, we seek to prepare students to create the next generation's physical chemistry, which implies the ability to derive new relations modeling physical-chemical phenomena on an “as needed” basis. This implies that the derivations that we do in physical chemistry are more than what they appear to be. They are intended to show students *how* modeling in the physical sciences is approached (they are also supposed to convince students of their correctness). It is the faculty's hope that students will emulate the derivation methodology in new, as yet undreamed of scenarios, with not only gusto, but confidence that their skills are adequate to the task.

### C. Third Justification

No matter what kind of chemistry one ends up doing (or biology, engineering, law, etc.), we hope that the larger picture of the transition from the micro to the macro world will be engraved in one's mind, so that one

obtains a *Gestalt* about the overview of science as it is currently understood. Even if the details evaporate, the structure, the relationships, should remain.

If, at some future time, quantum mechanics and/or statistical mechanics are supplanted by some as yet unknown mechanics, we assume that what we have learned so far will be included in the newer picture, in some limiting manner. No matter what the future, the ideas studied here will forever remain valid, even if limited by future developments.

### D. Fourth Justification (chemistry specific)

From the point of view of the thermodynamicist, thermodynamics is interesting *per se* and needs no justification. From the point of view of the ...; one can fill in whatever blank one wants here.

Clearly, specialists become enamored of their specialties, and teach those specialties as if they were the exclusively interesting subject in the world.

Chemists, by their very choice of chemistry as their discipline, are interested in reactions, specifically, chemical reactions, and from the larger point of view, these divide into those reactions that go to “completion” and those that attain some kind of equilibrium. This latter class is of interest here. How does a chemical system come to equilibrium?

- $G \rightarrow \min$  at fixed  $T$  and  $P$ . This leads to

$$\Delta G = \Delta G^\circ + RT \ln Q$$

which, when  $\Delta G \rightarrow 0$  yields the central chemical result

$$\Delta G^\circ = -RT \ln K_{eq}$$

- $G$  theoretically comes from the Helmholtz Free Energy ( $A$ ) which itself comes from the partition function ( $Z$ ), which comes from the set of energy levels which themselves have been obtained from the quantum mechanics of the situation at hand.
- $G$  experimentally comes from  $\Delta H$  measurements,  $S^\circ$  measurements, etc..

No matter how approached, chemical equilibrium and its attainment is the crown jewel of traditional Physical Chemistry.

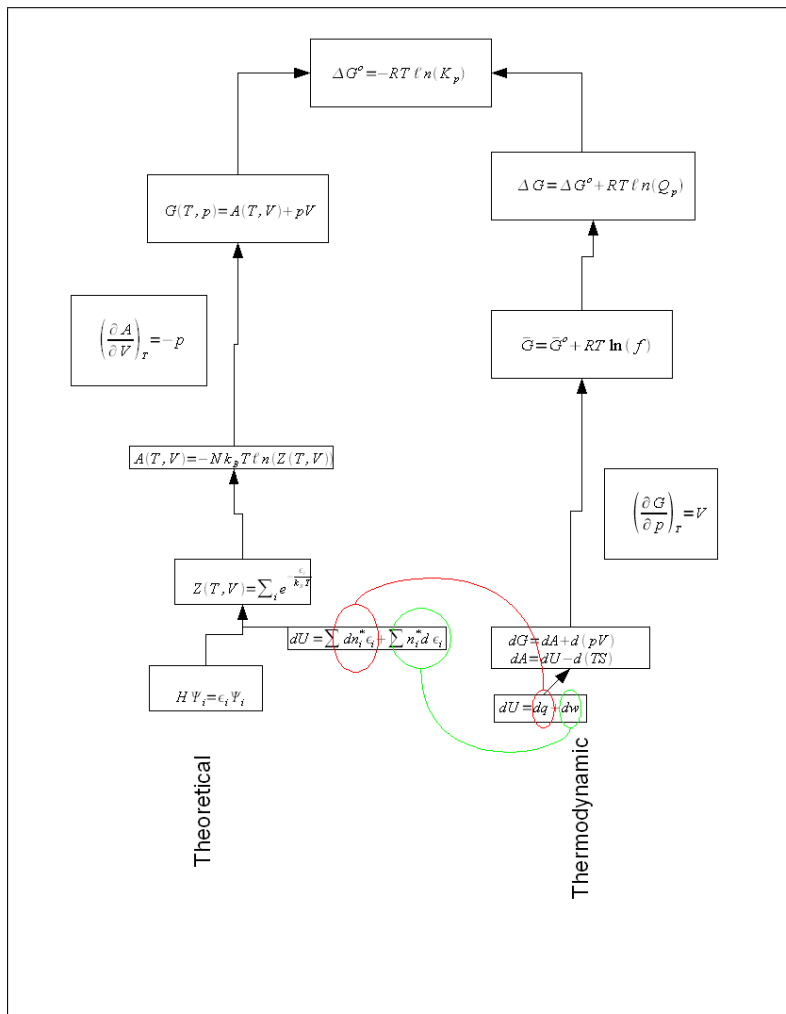


FIG. 1: Why Study Thermodynamics. If one follows the clockwise path from  $H\psi_i = \epsilon_i\psi_i$  to  $K_p$  versus the counter-clockwise path from  $dE = dq + dw$  one arrives at the same point.

### E. And then there was Spectroscopy, etc.

One must always keep in mind that the study of Physical Chemistry partly transcends thermodynamics and aesthetics. There are spectroscopic, structural, and chemical mechanistic reasons for studying all of these subjects in a Physical Chemistry environment.

And finally, in the true scientific nature of the endeavor, there is just plain simple curiosity concerning how things work in the chemical environment we are dealing with.

For any of these reasons, the study of theoretical chemistry may require some review of principals which come from different parts of the entire world of chemical theory but which illustrate the above comments. The following sections deal with these elements as a review.

### III. THERMODYNAMICS FROM STATISTICAL THERMODYNAMICS

We know that

$$S = k_B \ln W_{max} \quad (3.1)$$

where

$$W_{max} = \frac{N!}{\prod_i n_i^{\otimes}!}$$

in which the energy level occupation numbers ( $\{n_i^{\otimes}\}$ ) are those which describe equilibrium, i.e.,

$$n_i^{\otimes} = \frac{N e^{-\beta \epsilon_i}}{\sum_i e^{-\beta \epsilon_i}} \quad (3.2)$$



FIG. 2: The man

where  $\beta$  will become  $\frac{1}{k_B T}$ , *vide infra*. As usual, using Stirling's approximation, we have

$$\ln W_{max} = N \ln N - N - \sum_i (n_i^{\otimes} \ln n_i^{\otimes} - n_i^{\otimes}) \quad (3.3)$$

where we note in passing that

$$\sum_i n_i = N = \sum_i n_i^{\otimes}$$

(whether we are in the equilibrium state or not) results in a fortuitous cancellation. We add in passing that again

$$\sum_i n_i \epsilon_i = E = \sum_i n_i^{\otimes} \epsilon_i$$

for any set of  $n$ 's ( $\{n_i\}$ ) and for the equilibrium set ( $\{n_i^{\otimes}\}$ ). Substituting the equilibrium populations (Equation 3.2) into the occupation numbers of Equation 3.3 we obtain

$$\ln W_{max} = N \ln N - \sum_i \left\{ \frac{N e^{-\beta \epsilon_i}}{\sum_i e^{-\beta \epsilon_i}} \ln \left( \frac{N e^{-\beta \epsilon_i}}{\sum_i e^{-\beta \epsilon_i}} \right) \right\}$$

which is

$$\ln W_{max} = N \ln N - \sum_i \left\{ \frac{N e^{-\beta \epsilon_i}}{\sum_i e^{-\beta \epsilon_i}} (\ln N - \beta \epsilon_i - \ln Z) \right\}$$

which is

$$\ln W_{max} = - \sum_i N \left\{ (-\beta \sum_i \epsilon_i e^{-\beta \epsilon_i} - \ln Z) \right\}$$

where, of course,

$$Z \equiv \sum_i e^{-\beta \epsilon_i}$$

so that, using Equation 1, we obtain

$$S = k_B [\beta E + N \ln Z]$$

where, we know that  $\beta = \frac{1}{k_B T}$ .

Remember that the energy levels are functions of the length, area, or volume only if we are dealing with particles in 1, 2, or 3 dimensional boxes. Therefore, cross multiplying by T we have

$$TS = E + N k_B T \ln Z(V, T)$$

or

$$E - TS = -N k_B T \ln Z(V, T) \equiv A(V, T)$$

This fundamental identification of the Helmholtz Free Energy with the partition function shows that  $A$  (and  $Z$ ) are functions of temperature and volume. [1].

#### IV. AN EXAMPLE OF PARTITION FUNCTION EVALUATION

For a one dimension gas (where  $L$  will serve instead of  $V$ ), we know that the energy levels are given by the quantum mechanical formula

$$\epsilon_i = \frac{i^2 \hbar^2 \pi^2}{2mL^2}$$

Since the energy levels are themselves functions of the volume (here length,  $L$ ), it is apparent that when one substitutes these energy levels into the partition function that one generates a function of  $T$  and  $L$  (or  $V$ , if you will):

$$Z = \sum_i e^{-\beta \frac{i^2 \hbar^2 \pi^2}{2mL^2}}$$

Further, as all elementary treatments show (*vide ante*), this partition function leads to the average thermal energy being  $E = (1/2)N k_B T$  (i.e., assigning  $\beta = 1/T$ ), where, had we done the derivation in three dimensions, we would have had  $(3/2)N k_B T$ . This, of course, is a triumph of the statistical mechanical theory.

##### A. Temperature Identification

It may be worthwhile to remind the reader that the approximate evaluation of the partition function in this case results in the identification of  $\beta$  with  $1/k_B T$ , i.e.

$$Z = \sum_i e^{-\beta \frac{i^2 \hbar^2 \pi^2}{2mL^2}} = \sum_i e^{-\beta \frac{i^2 \hbar^2 \pi^2}{2mL^2}} (i+1-i) = \sum_i e^{-\beta \frac{i^2 \hbar^2 \pi^2}{2mL^2}} (\Delta i)$$

which, in standard calculus fashion, substituting an area for an integral when passing to the limit the  $\Delta i \rightarrow 0$ , we have

$$Z \approx \int e^{-\beta \frac{i^2 \hbar^2 \pi^2}{2mL^2}} di$$

which is a Gauss integral, eminently evaluable. From the (now) known expression for  $Z$  one obtains an expression for  $Z$ , and then  $G$  and then  $p$ , such that, recasting  $\frac{pL}{nR}$  one associates  $\beta$  with temperature.

## V. RE-INTERPRETING THE FIRST LAW OF THERMODYNAMICS

From thermodynamics, we had

$$dE = dq + dw$$

and from statistical thermodynamics we now have

$$E = \sum_i n_i^\otimes \epsilon_i$$

and we see that there are two ways to change the energy in this last expression, changing the energy levels themselves, or changing the occupation numbers. Thus

$$dE = \sum_i \{dn_i^\otimes \epsilon_i\} + \sum_i \{n_i^\otimes d\epsilon_i\}$$

The first term corresponds to reversible heat ( $dq$ ), and the second term corresponds to reversible work ( $dw$ ). It is little short of amazing that the extension of these ideas to irreversible processes results in the First Law,

$$dE = dq + dw$$

in exact correspondence with the reversible case. This miracle was noted nicely by Batino [2].

What a spectacular clarification. Keeping systems in their individual energy levels but allowing those levels to shift corresponds to external work of some kind. Keeping the energy levels fixed and shifting the populations of those energy levels corresponds to heating (or cooling).

Adiabatic processes correspond to processes in which the populations are maintained constant and equilibrium adiabatic (reversible) processes are those in which the equilibrium populations  $\{n_i^\otimes\}$  are maintained constant.

Heat addition (or subtraction) results in population changes, while work (either performing it or having it performed on the system) results in changes in the energy levels themselves.

## VI. INTERPRETING ENTROPY

The equation

$$S = k_B \ln W_{max}$$

forms the basis for our molecular (as opposed to thermodynamic) understanding of entropy [3]. If we are at an equilibrium state, and the exterior conditions change so that we end up at another equilibrium state, then the value of  $S$  guides us in understanding whether or not this process was spontaneous. Increasing entropy (associated with spontaneity) means that the number of states over which the systems are to be distributed has increased. The end state is more probable than the beginning state, when the probability is defined as the number of ways the systems can be distributed amongst their microstates in the two cases, before and after.

Consider a particle in a one-dimensional box of length  $\ell_1$  (this was  $L$  above). Fix the number of particles, fix the total energy, and distribute the particles amongst the energy levels consistent with that fixed (total) energy. Consider that there's a most probable distribution of particles amongst energy levels.

OK!

Now, allow  $\ell_1$  to become  $\ell_2$ , with  $\ell_2 > \ell_1$ . This corresponds to an expansion. Let's allow the change to occur with no flow of heat in or out of the system, i.e., adiabatic. Since this is an ideal gas, we know from the first law that the total energy does not change.  $dq = 0$ ,  $dE = 0$  and  $\int dE = 0$ . No work has been performed or obtained from the system, therefore when equilibrium is established after this free expansion, the particles have to be redistributed amongst the *new* set of energy levels (the number of particles has not changed!).

The energy levels have dropped, since  $\ell_2$  is in the denominator of the expression for the energy levels in the final situation.

There are more ways, now, of distributing the particles amongst the (new) energy levels than there were before.

There has been an increase in entropy! We've gone from one equilibrium state to another. But that makes no difference for  $\Delta S$ .

## VII. SUMMARY, SO FAR

This overview of the why and wherefore of relating classical thermodynamics to modern statistical thermodynamics (and an underlying quantum mechanics) is simplistic in some ways, since it, in essence, assumes the ideal gas state for every system. Thus, the real challenge

is not understanding this interrelationship between simple concepts in the several disciplines, but understanding instead the nature of the grotesque assumptions being made, which need to be undone before applying this work to “reality”.

Consider the linkage between quantum mechanics and statistical mechanics. Is the only use of this linkage possible when the Hamiltonian is a sum of uncoupled, individual Hamiltonians, implying a separation of energy terms using sums? If the assumption is not made that atoms interact independently in a system, say a system of Helium atoms, then the true Hamiltonian of the system consists of the Hamiltonian for all the nuclei *and* all the electrons. Since we can not, and most likely never will be able to, solve this enormous problem, it is usual practice that we solve the two problems separately, first say, solve the problem of the electronic energy levels of Helium’s electrons and second the quantum mechanics (or statistical mechanics) of the interaction of two, three, four, etc., Helium atoms, attempting to infer a scheme which allows us to bypass continuing these computations *ad nauseum* but instead, allows us to shift our attention from the Schrödinger equation to the partition function. Of course, breaking up the system into discrete atoms means we may have to invent three-body, four-body, etc., interaction terms, an artifice induced because the decomposition is false (but useful).

## VIII. THE THERMODYNAMICS EXAMPLE WHICH SHOWS THE PASSAGE TO EQUILIBRIUM

The passage to equilibrium from arbitrary starting points is a “central mystery” of elementary chemistry. A previous discussion (J. Chem. Ed., 65,407(1988), there is a typo in this paper) amplified, using a different example, to cement understanding can be found at [http://digitalcommons.uconn.edu/chem\\_educ/51](http://digitalcommons.uconn.edu/chem_educ/51).

## IX. CONCLUSIONS

So, there you have it. We’ve shown the relationship between quantum mechanics, statistical thermodynamics and classical thermodynamics, *and* offered a classical thermodynamic argument why chemical equilibrium comes about under the postulate that the Gibbs free energy seeks a minimum at constant  $T$  and  $p$ ; changing the extent of reaction allows the Gibbs free energy to change under these constraints so that one can find the minimum Gibbs free energy.

One can only hope that these arguments help in motivating our desire to master all of these topics.

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[1] Note that if we multiple and divide  $Nk_B$  by  $N_{Avogadro}$  we obtain the molecular form  $nR$ , where  $n$  is the number of moles and  $R$  is the familiar molar gas constant  $\frac{Nk_B N_{Avogadro}}{N_{Avogadro}} = nR$  since  $\frac{N}{N_{Avogadro}} = n$ .

[2] R. Batino, J. Chem. Ed., 84, 753 (2007).

[3] There is so much written about entropy that can be misleading to students, that I refer the reader to Frank L. Lambert, *J. Chem. Phys.* **76**, 1385 (1999) for an excellent statement about how to understand this concept