# A Short Essay on the Uses Of Free Energy

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**Abstract**

In this article we examine cases of more classical and less classical nature compared to results found by quantum mechanics and attribute a form of Free Energy discontinuity for each case within a boundary layer. The concept of a boundary layer is broadened as to include areas of first or second variations of the Gibbs free energy. It is constructive to think not only of implosions like boundary layers but also of explosion like ones. Situations such as boiling and the passage of electric current are compared and results are deduced. It is illusive that free energy contains a term proportional to the surface tension times the area.

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## Part I: Comparison of the Process at the Surface of Boiling of Water and the Process inside an Electrolytic Cell

In the discussion about the surface conditions in the boiling water in a paper written by Koutandos (2012) the limiting condition of the validity of the Bernoulli law having taken in mind an elimination of the Pressure at the side of vapor due to smallness of order of magnitude we make the following approximation as far as thermo dynamical quantities are involved is:

1) There is a difference of Pressure
2) There is a difference (jump) of densities at the two sides

The second condition accounts for a difference of Free Energy

$$\delta G/V = \mu \delta d \qquad (1)$$

It is also true that the difference of pressure between the gas and that of the bulk pressure of the liquid is associated with the surface pressure of the droplets:

$$P_g - P_l = \frac{2\sigma}{r} \qquad (2)$$

To a first approximation equation (1) evolves a steady chemical potential and this in turn means that the state at the surface is considered fluid as to the Van der Waal's electrostatic interactions but as shall be explained afterwards a perfect gas too.

This is Van der Waal's formula for a gas as is steam (Landsberg, 1978):

$$\left(P + \frac{N^2 a}{V^2}\right)(V - Nb) = Nk_B T \qquad (3)$$

The meaning of the Nb coefficient is an extra volume of the water droplets inside the gas and if this is dropped we deduce an amount of Pressure change simply accounting for the attraction between molecules (Landsberg, 1978)

The condition (1) for the layer reminds the condition of dissolution studied in Landau (Landau and Lifshits, 1959). It seems that this is necessary in the state of creation of mass of one fluid and annihilation of the other; so illusionary this – equation (1) – is the condition in the boundary layer of some kind of mass flow.

In electric cells on the other hand, there is the condition of sudden jump of the chemical potential, so

$$\mu=\mu_0+\delta\varphi \qquad (4)$$

$$\delta G/V=(\delta\mu)d \qquad (5)$$

That is, the condition in the electric case being the continuation of the current- unlike the case of boiling.

In an recent article (Koutandos, 2012), we used a modified Bernouli's law to find that the steam molecules are about 1000 times more energetic than water molecules as far as the square of the velocity is concerned and that accounts for a 30 times about bigger velocity of steam as to water molecules. The air molecules soon absorb this speed and the steam is partially condensed. In circumstances where water is in equilibrium with its steam however this amount of velocity can be brought to surface if we take in mind that in piping typical values of steam velocity is about 45 m/sec. This is about 30 times an amount of 1.5 m/sec of the water velocity. It is assumed that as layer is considered the whole of the steam just like we are going to use as a layer for the second variation of G the whole of the solid boundary.

One last comment to be added is that during boiling polarization forces are taken into account of the Wan der Waal's nature instead of purely ionic ones in the electrolytic cell.

## Part Ii: The Process of Exchange of Heat Between Boiling Water and a Heat Reservoir Compared to the Thermoelectric Effect

At the bottom of a can of boiling water (we may assume it is being heated with flames) we naturally have a layer – that of the wall of the can. There is definitely a temperature difference there but the temperature is being held constant in the water at $100^0$ C. Since the can is solid we have that its specific heat at constant volume is constant at $C_v$=3R. Now, there are implementations of this. First of all, within the walls we should have a temperature gradient plus a heat transfer. Supposing the heat capacity constant and nearly equal to the specific heat capacitance of constant volume and this is legitimate because of experimental facts we should have the following relationship:

$$\frac{\delta Q}{T}=\delta S=\frac{C_v\delta T}{T} \qquad (6)$$

There is also an expansion of volume yielding:

$$\delta V=\frac{1}{V}\frac{dV}{dT}\delta T=\alpha\delta T \qquad (7)$$

There is also a change of pressure according to the formula:

$$\delta P = \frac{VdP}{dV}\delta V = B\delta V \tag{8}$$

On combining equations (7) and (8) we get:

$$\delta P \delta V = \alpha B \delta T \tag{9}$$

While on the other hand:

$$\delta S \delta T \approx C_v \frac{(\delta T)^2}{T} \tag{10}$$

This reminds more or less the formula for heat diffusion given by Landau within a shell in terms of deltas (Landau and Lifshitz, 1959)

Equations (10) and (6) combined give:

$$\delta^2 G \approx \delta S \delta T - \delta P \delta V \approx C_v \frac{\delta T^2}{T} - \alpha B \delta T = C_v \frac{(\delta T)^2}{T} - \alpha B \frac{(T\delta T)}{T} \Rightarrow$$

$$\Rightarrow \delta^2 G \approx \frac{KT}{\left(\alpha B \frac{\delta T}{T} + C_V \left(\frac{\delta T}{T}\right)^2\right)} \tag{11}$$

Now, if we suppose that the variation of G to be connected with the variation of Omega, the function for the electrons obeying Fermi-Dirac distribution in analyzing it we obtain some results:

$$\frac{\delta \Omega}{\Omega} = -\frac{\delta(P_e V)}{P_e V} = -NK\frac{\delta T}{T} \tag{12}$$

First we confirm the validation of the results in that the number of electrons does not seem to change and that in assuming:

$$\frac{\delta G}{G} \approx \frac{\delta \Omega}{\Omega} \tag{13}$$

Then we may solve in a way equation (11) to find G. The phenomenon is purely one of transport. However electrons could be said to be the carriers of heat only as intervening to the vibration degrees of freedom of the solid.

Actually what should be noticed is that between the layers of double variation of G there are two other layers of variation? For this reason, where the combustion takes place we have:

$$(\delta G)_{combustion} = \mu \delta N \tag{14}$$

The so-called layer of double variation of G stabilizes the effect and could be said to be made of fluctuations.

However in the transport of current after the Galvan electrolytic cell the what might be called as layer and this would be the conductor (equal potential) has a double variation of N, for in such a case we might be talking of what is known as the “drift current” or else a diffusion current.

## Discussion

For part I some everyday evidence of the thermodynamic quantities that come into play in the two different instances could be used. We all know that after the batteries run out sometimes we feel them hot and this is the last bad attempt to draw some voltage of the system but it shows the difference of temperature that may be involved. On the other hand we are aware that a lot of vibration goes around during boiling and that may be due to fluctuations of pressure on a larger scale. Many degrees of linear turbulence like Faraday waves may be excited during the event.

At part II we found that there is a discontinuity, so to speak of, of the order of the second variation of the free energy. What this brings in mind is a second order phase transition. In the case of a second order phase transition there is usually a discontinuity of the specific heat but usually a continuity of the big thermodynamic quantities. For instance:

$$\delta C_V \approx \left(\delta^2 U\right)_V \approx \delta_V \left(\frac{TdS}{dT}\right) \qquad (14)$$

Most likely this could be attributed to a change in the order of heat transfer. This is because a second order phase transition is accompanied by what is called an order parameter. An example of this is superconductivity where electrons seem to create vortices below a threshold of temperature and magnetic field known as fluxions. Here the case is more of a turbulent motion.

One more thing about a vessel containing water and steam in equilibrium is that the pressure builds up of course and a simple analogy is that with a tank containing water where we open a hole at the bottom, the water will be exerted with some initial velocity.

## Experimental Apparatus

Regarding the boundary layer scheme we may reproduce the following experiment: If we boil some water and input a digital thermometer during its boiling in the glass jar the indication might be some $98.5^0$C while if the end point of the digital thermometer touches the bottom of the jar the indication will be again 100 degrees Celsius as expected.

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