

Flaw in Duncan's paradox

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Sheehan¹ recently discussed the possibility of existence of dynamically-controlled pressure or temperature gradient in black-body cavity. Duncan² proposed that if this pressure gradient exist and can be measured in laboratory then it will violate the 2nd law of thermodynamics. Sheehan et.al³ performed black-body cavity experiment by using tungsten and rhenium metals, H_2 and He as reactants in gas-surface interface reaction and claim that they have indeed measured the temperature difference (equivalent to the pressure difference according to their definition). In this paper we will discuss about the flaw that exist in Duncan's paradox and in Sheehan³ analysis. We will show that 2nd law of thermodynamics is still valid in their experiment.

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I. INTRODUCTION

Sheehans¹ recently published his work on the dynamically-controlled steady state pressure gradient in a black body cavity. He derives pressure difference on two very chemically deferent surfaces, S_1 and S_2 (see in figure 3). In his derivation the pressure differences are purely arises due to the different rate of dissociation and recombinations of chemical species A_2 and A in chemical reaction $A_2 \rightleftharpoons 2A$ on S_1 and S_2 surfaces. He claims that this dynamic pressure difference can be sustained in steady-states. Duncan² uses Sheehans¹ pressure difference claims and predict that if this pressure difference really sustain then one can make a perpetual machines like turbines with apposite blades which can use this pressure difference and generates a net torque, and thus in principle it can keep rotating for ever without any external work on the system. Sheehans et al.³ performed experiments using tungsten and rhenium as S_1 , S_2 surfaces (see in Figure 4) and claims that they have measured the temperature difference (equivalent to the pressure difference according to their definition) between the two surfaces. Sheehans et al.³ concluded (see conclusion section in³) that their result can not be explained under current framework of 2nd law of thermodynamics and thus 2nd

law of thermodynamics require a serious modification.

In this paper we will discuss the shortcoming that exist in Sheehans¹, Duncan² and Sheehans et al.³ papers. We will only discuss the inaccuracy that exist in these papers.

II. SHORTCOMING IN SHEEHANS PAPER¹

Sheehans¹ during his pressure difference ($\Delta P = P_1 - P_2$) derivation has completely ignored the momentum of adsorbed gases on both S_1 and S_2 surfaces. He assumes that gases adsorb on both surfaces with effectively zero momentum (see equation 18 in¹) or he assumed that, first gas get absorbed (less than mono-layer) and then he derived his pressure formula for desorb gases. This assumption is not valid for any equilibrium or non equilibrium process at any temperature and pressure. So equation 18 (see¹) has to be modified and includes at-least two extra term namely; pressure contribution due to molecule A_2 adsorption on S_1 surface, and pressure contribution due to atoms A adsorption on S_2 surface (see in Figure 1). So, two extra terms, $m_{A_2}v_{A_2}R_{ads}(1, A_2)$ and $m_Av_A R_{ads}(2, A)$ should have been added in equation 18 (see in¹). In this equation R_{ads} stands for rate of adsorptions of chemical

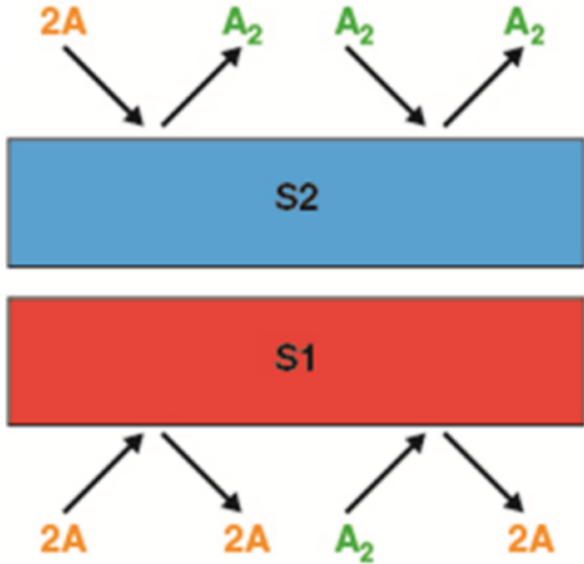


FIG. 1: proposed Duncan's device set-up³.

species on the corresponding surfaces in per-second and in per-meter-square surface area. So, the final equation should have been written as,

$$\Delta P = m_A v_A R_{des}(1, A) + m_{A_2} v_{A_2} R_{des}(1, A_2) + m_{A_2} v_{A_2} R_{ads}(1, A_2) - m_A v_A R_{des}(2, A) - m_{A_2} v_{A_2} R_{des}(2, A_2) - m_A v_A R_{ads}(2, A).$$

At any temperature and pressure R_{ads} term should have been added on both S_1 and S_2 surfaces. It does not matter that whether reaction is in equilibrium or in non-equilibrium. If R_{ads} terms drop in equation 18 (see in¹), then there is no reason to believe that why R_{des} term should not be dropped, because adsorption and desorption is a thermodynamic process and it occur simultaneously in both equilibrium and in non-equilibrium situation. Only the rate constant term for the adsorption and the desorption process shall be different in chemical reaction $A_2 \rightleftharpoons 2A$ at S_1 and S_2 surfaces when reaction move in either forward or in backward direction.

III. SHORTCOMING IN DUNCAN PAPER²

Duncan in his paper² thought that pressure difference on two surfaces (see for example S_1 and S_2 surfaces in figure 2) can rotates the turbine blades. He ignores that if there is net pressure difference on any system then there will be net force ($\Delta P \times A$, where A is the surface area of S_1 or S_2) on the system center of mass. So system will not only rotates but translates as well. This system is very unstable in translational degree of freedom. So in this system no process will be cyclic and regain it original thermodynamics states after one complete rotation. Also the one part of total chemical energy of the system has been used to rotates the blades (rotational kinetic energy) and the other part of the chemical energy has been used for the translational kinetic energy of the center of mass of the system. If one assume that there will be some kind of holder which hold the turbines shaft, so that it can not translate, then there will be a frictional force which arise between the holder and in turbine shaft. Then shaft will rotates against this frictional torques and thus a part of the chemical energy will waste against irreversible frictional work. If one think an ideal holder which does not generate a frictional torque between the holder and in turbine shaft, then it will be a complete absurdity because there will always a frictional force and thus frictional torque between any two material media. The frictional force arises due to quantum mechanical effect. Only static/kinetic frictional coefficients value can be minimized but it value can never become complete zero. Now let see what Planck- Kelvin statement says about the second law of thermodynamics:

“The KelvinPlanck statement (or the heat engine statement) of the second law of thermodynamics states that it is impossible to devise a cyclically operating device, the sole effect of which is to absorb energy in the form of heat from a single thermal reservoir and to deliver an equivalent amount of work. This implies that it is impossible to build a heat engine that has 100% thermal efficiency”⁴.

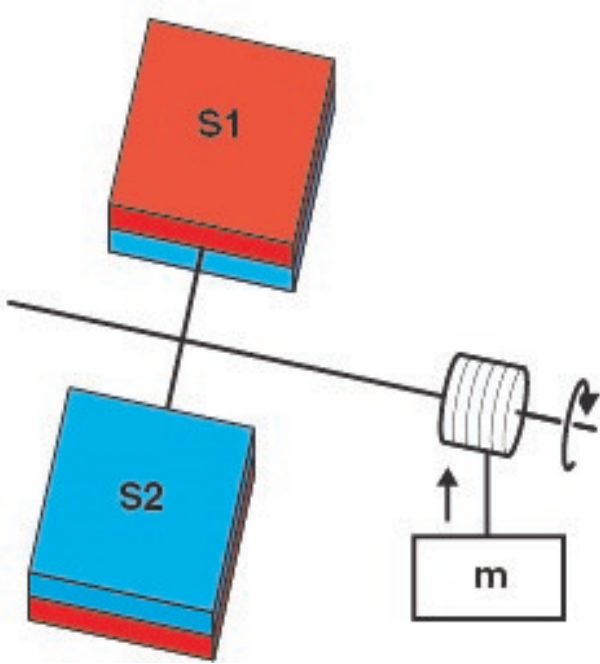


FIG. 2: proposed Duncan's device set-up³.

The first key point in Kelvin-Planck statement is the “*cyclically operating device*”. Second key point is “*100% thermal efficiency*”. Duncan's device is irreversible non-cyclic device. Also Duncan's device is not 100% efficient, because only a fraction of the total chemical energy has been used in rotational process. Other part of chemical energy has been used in translational process. So *useful mechanical work* (for example lifting weight) will always be less than 100% available chemical energy. Therefore, no question of breaking the 2nd law of thermodynamics arises in Duncan's paradox.

IV. SHORTCOMING IN SHEEHANS ET AL. PAPER³

There are number of shortcomings in this paper. We will go one by one. Sheehans et al.³ claims that they have measured two different temperature on tungsten and rhenium metal surfaces in their black body cavity experiment (see in Figure 4). Since tungsten and rhenium are two different metals, they also have different crystal structure, different Brillouin zones, different elec-

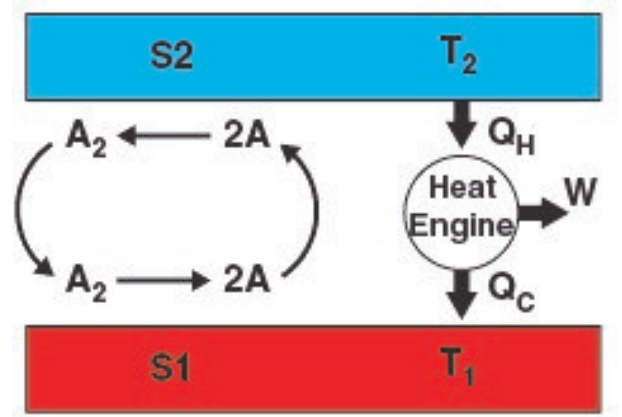


FIG. 3: Proposed chemical reaction on S_1 and S_2 surfaces³.

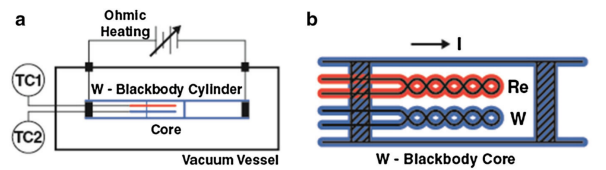


FIG. 4: Chemical reaction on tungsten (W) and rhenium (Re) surfaces in black body cavity³.

tronic and phonon band-structures, different surface orientations and different surface activation energy, therefore, one should not be surprised if tungsten and rhenium show different adsorption and desorption rates for the same gas (He , and H_2 in this case). Also, dissociation and recombination reactions are endothermic and exothermic respectively, whose rates are material, temperature, pressure, and surface specific, therefore, one should not be surprised if two different temperatures develop in the vicinity of two different metal surfaces. Also, the development of different temperatures in the vicinity of two surfaces does not guarantee that a pressure difference will also be developed. Because if one uses the ideal gas equation for pressure $P = \frac{\rho RT}{M}$, then one notices that pressure is not only dependent on temperature but also on density and molar mass of the mixture gases. So one needs to calculate the density of the gases and their effective molar mass in the vicinity of two metal surfaces (S_1 and S_2) before reaching any conclusion. Also, one mole of A_2 gas dissociates and forms 2 moles of A gas, so one must know the

degree of the chemical reaction α , for $A_2 \rightleftharpoons 2A$ in forward direction and rate constant to get the density and effective molar mass of the mixture gases. Because, on S_2 surface (see in Figure 3) $2A$ atoms combines and form A_2 molecules. So, at S_2 surface density of gas decreases and probably effective molar mass increases, but since reaction is exothermic, therefore, temperature of the gas in the vicinity of S_2 surfaces will increase as well. Since gas pressure equation (take ideal gas equation) $P = \frac{\rho RT}{M}$ is directly proportional to density and temperature but inversely proportional to the effective molar mass of the gases, therefore, it is extremely difficult to suggest or conclude that the gas pressure will also be different in the vicinity of two metal surfaces where the chemical reaction are taking place.

Let focus on Sheehans et al.³ paper:

(1), Sheehans et.al wrote “*Duncan argued that if these surface-specific chemical activities were indeed possible, then stationary pressure gradients could arise between the radiometers apposing vane faces that could, in principle, be used to create a pressure engine that performs work perpetually at the expense of the surrounding heat bath, in conflict with the second law of thermodynamics*”

Strictly speaking this statement is not correct because net pressure ($\Delta P = P_1 - P_2$) will also give net force ($\Delta P \times A$, where A is the surface area of the surface S_1 or S_2 , see in figure 2), and thus whole setup will have translational degree of freedom, and thus very unstable (we have discussed it in previous section).

(2), “*Because the filament pair has identical dimension, comparable emissivities and coefficient of thermal conductivity, their radiative and conductive loss were similar*”

Rhenium has *hcp* and tungsten has *bcc*-crystal structures. Both have different crystal lattice parameter and different surface orientations. Both have different electronic and phonon band-structures. electron and phonon band structures plays a very key role in electrical and in thermal conductivity. We don't know on what fundamen-

tal basis Sheehans et.al³ have concluded that they share *similar* properties except that they are only metals. Different metals have very different surface orientation, surface area and surface activation energy on microscopic level where reaction takes place. Origin of physical and chemical properties of any material is purely arises due to quantum mechanical effects.

(3), “*According to standard thermodynamics, it is required for all temperature and pressure that $\Delta T_{He}=0$ and $\Delta T_{H_2}=0$, but especially that $\Delta T_{H_2-He} = 0$, this is the crux of Duncan's paradox*”

Strictly speaking, this statement is only correct when both filament are made from same material. If both filament are made from the different materials as in Sheehans et al.³ case (W and Re), then thermodynamics does not says that $\Delta T_{He}=0$, $\Delta T_{H_2}=0$ and $\Delta T_{H_2-He} = 0$. In fact thermodynamics says that for any system macroscopic average value of $\langle \Delta T_{He} \rangle$, $\langle \Delta T_{H_2} \rangle$ and $\langle \Delta T_{H_2-He} \rangle$ should be zero. In other words, $\langle \Delta T_{He} \rangle=0$, $\langle \Delta T_{H_2} \rangle=0$ and $\langle \Delta T_{H_2-He} \rangle=0$ for any thermodynamical system. In this case the whole cavity should be treated as system, because surface coverage in cavity is very low (less than mono-layer). And due to extremely low gas pressure inside the cavity the thermodynamics rules are not applicable until one takes whole cavity as a thermodynamic system. Thermodynamics always talk about macroscopic average of any thermodynamics variable rather than few atoms or molecules. For example, temperature of one atom or one molecule does not make any sense, but temperature of few hundred thousands atoms or molecule does make sense.

(4), “*Thermal conductivity of helium is similar to that of H_2 and therefore can be used to estimate the convective loss in H_2* ”

Thermal conductivity of *He* and H_2 are same on every crystal structure and every surface orientations? Answer is absolutely “*No*”. *W* and *Re* have different crystal structure, different lattice parameters and different surface orientations. Also, geometrical surface area is not

the same as the microscopic surface area where adsorption and desorption are taking place unless both surface are made from same material.

(5), “it also indicate that the concentration of H and H_2 over two metals could not both have reflected gas-phase equilibrium value because equilibrium concentrations are unique for given temperature and pressure”.

Concentration is a macroscopic quantity and only average value of concentration in a certain volumes make thermodynamical sense. So, in principle surface concentration should not reflect the equilibrium concentration.

(6), “The difference in hydrogen dissociation power between the two metal-coated thermocouple was relatively small, but their difference in power density was substantial $\simeq 50 \frac{Kw}{m^2}$. If this temperature difference were employed in a classic heat engine, its Carnot efficiency would be low but thermodynamically significant”

If one see figure 3, then one notice that at S_1 surface endothermic reaction, whereas on S_2 surface exothermic reactions are taking place. Lets take temperature of the system T_s . Then at S_1 surface heat energy get absorbed by the A_2 molecule and dissociate into $2A$ atoms. If this reaction perpetuate and there is no heat flow from the external agency (which maintained the system temperature at a fix value), then S_1 surface will be cool down and its temperature moves toward zero kelvin in temperature scale. One should also know that the endothermic reaction is temperature dependent. Once temperature goes down then endothermic reaction will stop. Since S_1 surface temperature maintained at T_1 , it suggest that there is a competition between thermal energy that come from external agency towards surface S_1 , and consumed in the chemical reaction $A_2 \rightleftharpoons 2A$ by the A_2 molecules to get dissociation into $2A$ atoms. So, indirectly it is the external agency which maintained the S_1 surface temperature. Secondly, at S_2 surface, there is heat flow from the S_2 surface towards the external world through surface-coated tungsten wire (see in Figure 4). And thus S_2 surface temperature maintain at T_2 . Therefore, temper-

ature at S_1 and S_2 surfaces are maintained by the external agency. One should not confused that heat releases at the S_2 surface get consumed at the S_1 surfaces. There is no-way through this is possible in any system. Surface S_1 maintains its temperature by taking the heat energy come from the external agency which maintained the system temperature and pressure at a fix value. It seems to the author that Duncan² has thought that heat energy released at S_2 surface can be used at the S_1 surfaces during the endothermic reaction.

(7), “if the standard theory of heterogeneous catalysis is valid, then the GF filament should not have been able to shift their H and H_2 concentrations so far from equilibrium as was observed and not to distinctly different value in which case they should not have been able to display different hydrogen dissociation power consumption (P_{hd}). This implies that ΔP_{hd} should have been zero over entire temperature, pressure range investigated”

This statement is only correct if both filaments are made from the same material. In this case one filament is made from tungsten which has *bcc*-crystal structure and other filament rhenium has *hcp*-crystal structure. Both have different lattice parameters, different Brillouin zones, different electronic and phonon bands, different surface reactivity and different surface activation energies. One should not expect that they will behave exactly the same until they are perfectly identical in every aspects.

(8), “This argument fails on at-least two count, first, a standard formulation of the second law, one not requiring heat engines, stipulates that isolated system (like a black body core) must relax to an equilibrium characterized by single temperature. The experimental DP system did not, rather, it maintained two distinct temperature that did not-and apparently could not-relax to a single temperature on account of its dual surface-specific reaction rates. Apparently, the DP system constitutes a stationary-states non-equilibrium

First of all temperature is a macroscopic thermodynamic variables. Macroscopic thermodynamic variable always

calculated by using the macroscopic average statistical rules. So, getting one value in macroscopic average calculation does not mean that same value is present all over the place in macroscopic volumes. It only suggest that the calculated value is the average value. So, standard thermodynamics does not says that same temperature should be present on both S_1 and S_2 surfaces. It says that if both the filaments (S_1 and S_2 surfaces (see in figure 2) are made from the same materials) are same then the average temperature on both the surfaces should be the same, and it should be equal to the system temperature which is fixed by the external agency.

V. CONCLUSION

In this paper we have addressed the flaw that exist in Duncan's paradox. We have shown that the dynamically-

controlled steady-state pressure gradient or temperature-gradient is maintained by the external agency which controls the temperature and pressure in the black-body cavity. We have shown that the experiment done by Sheehen et al.³ does not violate the 2nd law of thermodynamics. We hope that this paper will clear the doubt about Duncan's paradox and stimulate the scientific community to start looking the physical observations at microscopic levels.

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¹ D. P. Sheehan, Phys. Rev. E, **57**, 6660 (1998)

² Todd L. Duncan Phys. Rev. E, **61**,4661 (2000)

³ D. P. Sheehan, D. J. Mallin, J. T. Garamella, W. F. Sheehan, Found Phys, **44**,235 (2014)

⁴ https://en.wikipedia.org/wiki/Kelvin%E2%80%9993Planck_statement