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SCIENTIFIC INVESTIGATIONS OF GRAVITATIONAL-EFFECTS ON FIRST LAW OF THERMODYNAMICS

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Abstract:

The first law of thermodynamics applicable to closed process or non-flow process system undergoing equilibrium state change in its present form does not consider the effect of gravity during equilibrium state change. In this work an analytical study have been carried out to find gravitational effects on the first law of thermodynamics, applicable to a system experiencing equilibrium state change. The first law of thermodynamic is not only a state function. It also depends upon the path followed by the process. The nature of the path will determine the effect of the gravitational force on the working fluid. The gaseous fluids due to scattered molecular pattern in comparison to liquids experience lesser gravitational effect than liquids. The Vander Waal's forces may also responsible for the same.
Key words- *First law of thermodynamics, Cyclic process, Equilibrium state, State function, Gravitational, Stored energy, Hidden energy, Reversible process.*

Introduction:

Mathematical Analysis of First Law of Thermodynamics

Total energy of an isolated system in all its form remains constant. Energy cannot be destroyed rather it can be converted from one form to another form of energy. - Boles, [M.A. (2003)] Let us consider a thermodynamic system (Figure-1), in which liquid metal (mercury) has been chosen as the working fluid instead gas or steam. The liquid metal atoms remain more closely in the liquid crystal and experience gravitational-effect more readily than a gas. A gaseous fluid due to intermolecular interaction and other relevant forces do not appeal toward gravitational-effect than a liquid-metal. The effect of gravitational work Wg on thermodynamics fluid during its expansion and compression cannot be ignored.

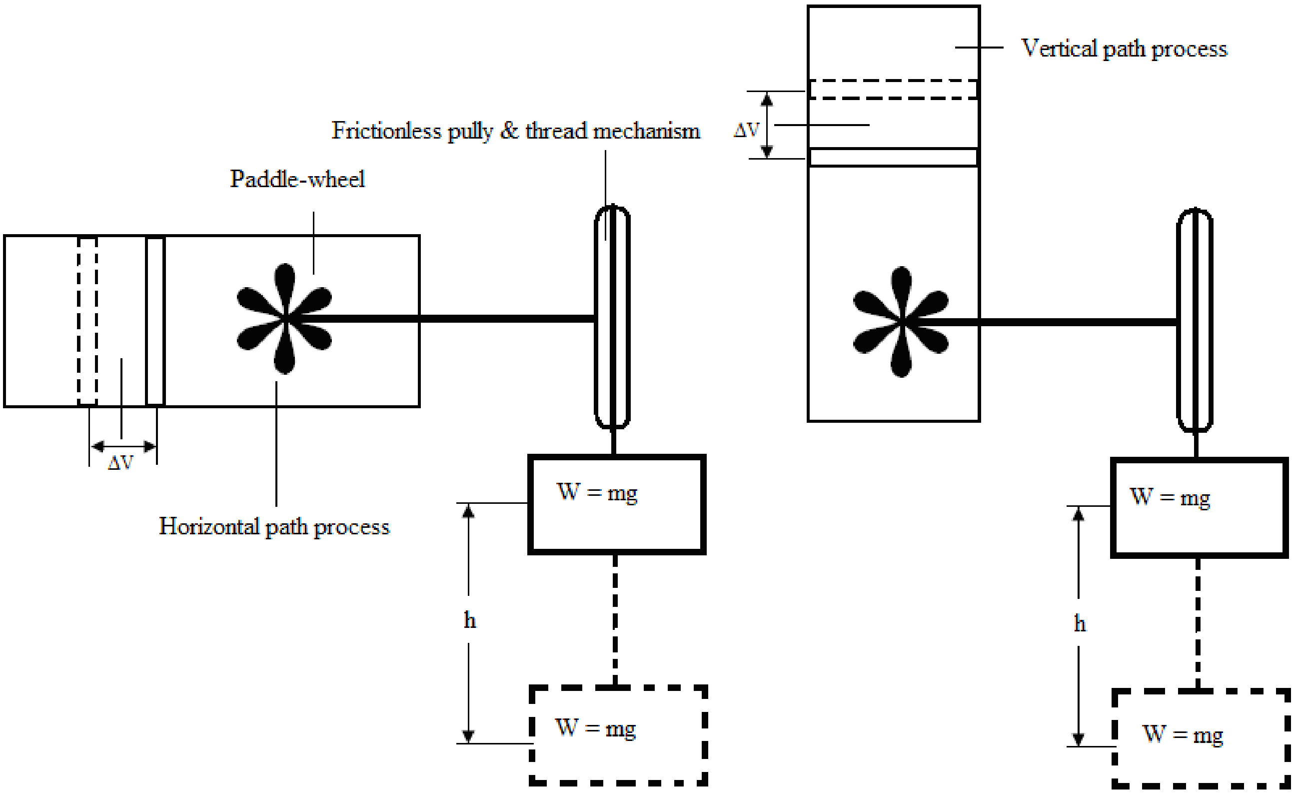

Figure-1

The cylinder is filled with liquid-metal, being the thermodynamic fluid. A paddle-wheel mechanism shown in Figure-1 is considered for theoretical investigations of this system. Let the frictionless paddle-wheel mechanism is run on the thermodynamic fluid for a fixed amount of potential energy (say mgh) transfer to the fluid (refer P-V diagram Figure-2 below).

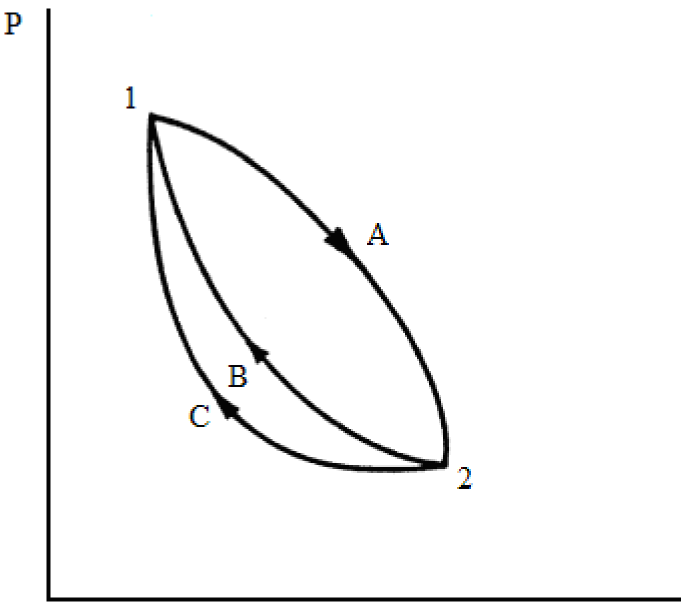

Figure-2

As per the first law, the cyclic integration of the heat developed due to mechanical work of paddle-wheel is equal to the cyclic integration of work W performed on the working fluid due to fall of the weight mg through a height of 'h' distance. Mathematically;

$$\oint \delta Q = \oint \delta W \quad \ldots 1$$

Or

$$\oint \delta Q - \oint \delta W = 0 \quad \ldots 2$$

Energy as Property of the System

[Walker (2004)], let the system goes under infinitesimal equilibrium process as shown by the P-V diagram below. The expansion of the thermodynamics fluid from equilibrium state-1 to equilibrium state-2 takes place through path 1-A-2. The compression of the thermodynamics fluid due to heat rejection from equilibrium state-2 to original equilibrium state-1 during return takes place via any of the arbitrary process given below;

i) Along path 2-B-1 or ii) Along path 2-C-1

Let both the equilibrium process path occur in a horizontal plane. It means that the nature of the system is such that the piston moves to and fro in a horizontal plane to the earth surface. Applying first law of thermodynamics to cyclic process 1-A-2-B-1 between equilibrium state-1 and state-2.

$$\oint (\delta Q - \delta W) = 0 \quad \ldots 3$$

The above equation can be divided into parts and can be re-written as follows;

$$\int_{1,\ \text{Via A}}^{2} (\delta Q - \delta W) + \int_{2,\ \text{Via B}}^{1} (\delta Q - \delta W) = 0 \quad \ldots 4$$

Or,

$$\int_{1,\ \text{Via A}}^{2} (\delta Q - \delta W) + \int_{2,\ \text{Via C}}^{1} (\delta Q - \delta W) = 0 \quad \ldots 5$$

Comparing equation (4) and equation (5)

$$\int_{2\text{, Via B}}^{1} (\delta Q - \delta W) = \int_{2\text{, Via C}}^{1} (\delta Q - \delta W) = 0 \quad \dots 6$$

Or,

$$\int_{2}^{1} (\delta Q - \delta W) = 0 \quad \dots 6^{*}$$

Or,

$$(\delta Q - \delta W) = dE \quad \dots 6^{**}$$

Equation- (6) provide a basic background for the first law of thermodynamics which states that the value of the integral $\int_2^1 (\delta Q - \delta W)$ remains constant irrespective of the path along which this system proceeds. This solely depends upon the initial and final states of the system and is a point function not a path function. This integral is known as energy of the system and is represented by letter E.

Analysis of Gravitational Effect

Since E is a property of the system. Its differential is exact and is denoted by dE. And the nature of the processes is horizontal to the earth surface so the gravitational work Wg = mg δl cos90° = 0, because cos90° = 0. Here, m is the mass of the thermally expanded volume ΔV and δl is the length of the expanded volume. In another investigation let's take all the processes of cycle 1-A-2-B-1 occur in a vertical plane. It means that the nature of the system is such that the piston moves up and down in a vertical plane to the earth surface. However the initial equilibrium state-1 and the final equilibrium state-2 are the same. The expanded/contracted volume ΔV of the thermodynamics fluid during its expansion and contraction undergoes a gravitational work Wg. This work cannot be neglected as per the first law conception about the principle of the conservation of energy. It can be explained such that the work is done by the expanded fluid volume (ΔV) on expense of thermal energy against gravitational work Wg (mg δl cos180°). The same work Wg (mg δl cos0°) is returned back during contraction of the expanded volume. Applying first law of thermodynamics on this vertical path cyclic process;

$$\oint \delta Q = \oint \delta W + \rho\, \Delta V\, g\, \delta l \cos 180^\circ + \rho\, \Delta V\, g\, \delta l \cos 0^\circ \quad \dots 7$$

Or,

$$\oint (\delta Q - \delta W) - \rho\, \Delta V\, g\, \delta l \cos 180^\circ - \rho\, \Delta V\, g\, \delta l \cos 0^\circ = 0 \quad \dots 8$$

The above equation (8) can be divided into parts and can be re-written as follows;

$$\int_{1\ ,\ \text{Via A}}^{2} (\delta Q - \delta W) + \rho\ \Delta V\ g\ \delta l \cos 180° + \int_{2\ ,\ \text{Via B}}^{1} (\delta Q - \delta W) + \rho\ \Delta V\ g\ \delta l \cos 0° = 0 \quad \ldots 9$$

And

$$\int_{1\ ,\ \text{Via A}}^{2} (\delta Q - \delta W) + \rho\ \Delta V\ g\ \delta l \cos 180° + \int_{2\ ,\ \text{Via C}}^{1} (\delta Q - \delta W) + \rho\ \Delta V\ g\ \delta l \cos 0° = 0 \quad \ldots 10$$

Comparing equation (9) and (10) produces same result as given by equation (6). It is concluded from the above equations that gravitational work Wg do not affects the first law of thermodynamics provided both the cyclic process 1-A-2-B-1 or 1-A-2-C-1 follows same nature of paths i.e. either vertical or horizontal.

Investigating Effects of the Nature of the Path followed by a Reversible Process

[N Shapiro (2000)] let's investigate the same paddle-wheel process 1-A-2-B-1 between equilibrium state-1 and equilibrium state-2. The expansion of the thermodynamics fluid from equilibrium state-1 to equilibrium state-2 takes place through a horizontal path 1-A-2. The compression of the thermodynamics fluid due to heat rejection from equilibrium state-2 to original equilibrium state-1 during return takes place via any of the arbitrary process given below;

ii) Along path 2-B-1 ii) Along path 2-C-1

The nature of the path 2-B-1 is horizontal and the nature of the path 2-C-1 is vertical. In this investigation although equilibrium state-1 and equilibrium state-2 remains same as per the previous investigation but nature of the paths (1-A-2 horizontal, 2-B-1 horizontal and 2-C-1 vertical) is different. Applying first law of thermodynamics to the above cyclic process 1-A-2-B-1;

$$\int_{1\ ,\ \text{Via A}}^{2} (\delta Q - \delta W) + \int_{2\ ,\ \text{Via B}}^{1} (\delta Q - \delta W) = 0 \quad \ldots 11$$

Or,

$$\int_{1\ ,\ \text{Via A}}^{2} (\delta Q - \delta W) + \int_{2\ ,\ \text{Via C}_{\text{verticle}}}^{1} (\delta Q - \delta W) + \rho\ \Delta V\ g\ \delta l \cos 0° = 0 \quad \ldots 12$$

Comparing equation (12) with equation (4);

$$\int_{2\text{ , Via B}}^{1} (\delta Q - \delta W) = \int_{2\text{ , Via C verticle}}^{1} (\delta Q - \delta W) + \rho\, \Delta V\, g\, \delta l \cos 0° \quad ... 13$$

Comparing equation (12) with equation (5);

$$\int_{2\text{ , Via C}}^{1} (\delta Q - \delta W) \neq \int_{2\text{ , Via C verticle}}^{1} (\delta Q - \delta W) + \rho\, \Delta V\, g\, \delta l \cos 0° \quad ... 14$$

But according to equation (6);

$$\int_{2\text{ , Via B}}^{1} (\delta Q - \delta W) = \int_{2\text{ , Via C}}^{1} (\delta Q - \delta W) = 0 \quad ... 6$$

The equation (14) concludes that integral $\int_{2}^{1} (\delta Q - \delta W)$ is not constant for all the return paths i.e. horizontal path 2-B-1, and vertical path 2-C-1.

State versus Path Function

Hence the first law of thermodynamic is not only a state function. It also depends upon the path followed by the process. [Freedman (1998)] For instance if at any point the nature of the path changes from horizontal to vertical or vice versa than the effect of gravitational work Wg cannot be ignored. Therefore the first law is not always valid in the present form. The amount of energy $\rho\ \Delta V\ g\ \delta l\ \cos 180°$ or $\rho\ \Delta V\ g\ \delta l\ \cos 0°$ always remains hidden, however it is always present during expansion and contraction processes of a thermodynamics system. But the net overall effect of this hidden energy is zero for the same nature processes, because the energy is conserved (refer equations 9 and 10). [B. N. Roy (2003)] the following information is obtained;

I - If all the processes occur in horizontal path than;

$$\int_{2}^{1} (\delta Q - \delta W) = 0 \quad ... 15$$

II - If expansion process follows a horizontal nature of path and compression process follows a vertical nature of path than;

$$\int_{2}^{1} (\delta Q - \delta W) + \rho\, \Delta V\, g\, \delta l \cos 0° \neq 0 \quad ... 16$$

III - If expansion process follows a vertical path and compression process follows a horizontal path than;

$$\int_{2}^{1} (\delta Q - \delta W) + \rho \, \Delta V \, g \, \delta l \cos 180° \neq 0 \quad \text{... 17}$$

IV - If all the processes follows a vertical nature paths than;

$$\int_{2}^{1} (\delta Q - \delta W) = 0 \quad \text{... 15}$$

[Van Whylen (2004)]With reference to the Figure-3 below, let's the system possessing a state-1 is subjected to a cyclic process 1-A-2 to reach a state-2. This process 1-A-2-is carried out via a vertical path. During this expansion process Q1 heat is added to the system and W1 work is done by the system.

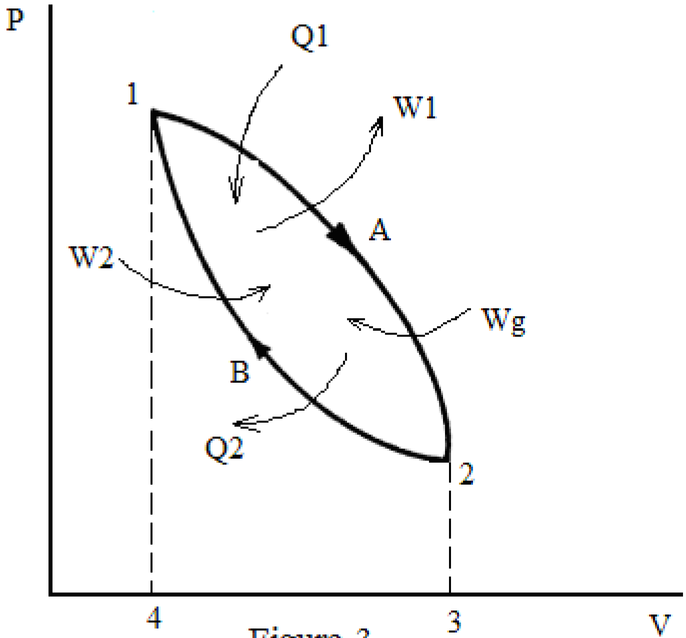

Figure-3

The gravitational work Wg is done on the expanding volume ΔV of the thermodynamics fluid (mercury). This work is stored in the form of potential energy in the expanded volume. The state-1 is restored in the system via a horizontal process 2-B-1. During this compression process W2 work is done on the system which produces heat Q2 within the system. Since this process is taken horizontally, so the amount of gravitational stored energy Wg do not appear in the process when initial state-1 is restored in the system. Applying first law of thermodynamics to this system;

$$(W1 - W2) - Wg = Q1 - Q2$$

$$\oint (\delta Q - \delta W) = - Wg \quad \text{... 18}$$

Concluding Remarks and Discussions

[Richard H. Dittman (1997)], as per the above investigations on the first law of thermodynamics using liquid-metal, the following remarkable conclusions can be drawn:

1- The effect of the gravitational work cannot be ignored during formulation of the first law of thermodynamics. Basically a thermodynamics expansion or compression process is represented on a P-V diagram. Apart from pressure and volume change the effect of gravity also influence the process. The integral referred in equation (6*) is not always a state function. It may also depend upon points of the paths nature during the cyclic processes. If the path changes its nature from horizontal to vertical or vice versa than the equation (6*) and equation (6**) of the system cannot be expressed in there's present form. The gravitational effect Wg cannot be ignored. The equations become as follows;

$$(\delta Q - \delta W) = dE \pm W_g \quad \text{... 19}$$

2- If all the paths follow same nature of processes either horizontal or vertical during a cyclic process between equilibrium state-1 and equilibrium state-2 the equation (15) remains valid. This is the present form of the first law.

3- If nature of the paths during any process of the cycle changes than either of the equation (16) and / equation (17) will be valid.

4- Thermodynamics equilibrium state is the condition of the system described by its properties such as pressure, volume, temperature and gravitational effect etc at a particular moment of the process under consideration. The gravitational works Wg cannot be ignored as this is a point function on a path and do not depend on initial and final state of the system.

5- When a system passes through the continuous series of equilibrium states during a change in its thermodynamic properties from initial state-1 to final state-2, then it is known as path of change of state. A path of a thermodynamic process can experience change in the volume, pressure, temperature and gravitation-effect. The gravitational effect is an extensive property.

6- Heat δQ is an inexact differential as $\int_1^2 \delta Q$ is not a point function. But gravitational work Wg is point function since;

Wg = $\rho\ \Delta V\ \delta l\ g \cos 180°$ / or $\rho\ \Delta V\ \delta l\ g \cos 0°$ is function of a point of ΔV on a path where gravitational work can appear at one particular point-moment and can disappear at other point-moment of the path.

7- The equation (18) has a very remarkable conclusion on the first law of thermodynamics. If nature of the thermodynamic process changes from vertical path to horizontal path or vice-versa at a particular expansion / or compression path, than gravitational work Wg become hidden or get disappear at end of the cycle. At a first instance the equation (18) showing –Wg amount of stored energy which got destroyed during vertical path process 1-2-A. But this will be violation of the first law of thermodynamics which states the energy can neither created nor destroyed. This amount of energy i.e. –Wg is given a name of hidden energy.

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