THE IDEAL GAS EQUATION $p = \alpha u$ AND THE ENERGY – ENTROPY PRINCIPLE

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ABSTRACT

The fundamental aim of this article is to show that, by considering an ideal gas defined through $p = \alpha u$, this relation between force and energy contains the whole thermodynamic information about the system. As a matter of fact we show that there is no need for an a *priori* introduction of the variables temperature or entropy since they result from the above relation and from the Energy Conservation Principle. Previous tautological treatments are thus eliminated and equations $p = \alpha u$ and $pV = BT$ are related with generality. The theory is general since the ideal gas considered has the photon gas, which, of course, is ever present.

1. INTRODUCTION

The relation between $p = \alpha u$, and the other pressumed thermodynamic quantities have already been treated in the literature (Uhlenbeck 1932, London 1938, Einbinder 1948, Einbinder 1949, Miller 1960, Landsberg 1961, Landsberg 1974).

We shall, however, demonstrate that when $p = \alpha u$, it is possible to associate temperature with energy through the relation $U = AT$ where A is constant along the isentropic transformation.

An ideal gas therefore satisfies $pV=BT$ and if B is approximately constant along an isothermal line, then the gas behaves like a classical ideal gas.

The preceeding statements can be demonstrated through a generalization of Carnot's theorem (Abreu 1983) which permits an easy interpretation of the relations arising from Energy and Entropy. This generalization makes it possible to treat in the same way a photon gas or another Bose-Einstein or Fermi-Dirac gas, the reasoning that led Boltzmann to the deduction of Stephan's law having been used in a similar way. With this synthesis we can achieve a great simplicity and previous tautologies are eliminated. In VIII, and in a more abstract way, the formalism which condenses the relations previously established is directly obtained from $U=U(S,V)$.

2. ENTROPY and $p = \alpha u$

The relation $p = \alpha u$ shows that if pressure increases, the energy density increases as well.

This being the case, if the gas (Abreu 1987) follows a trajectory in the domain of variables p and V coming back to its initial volume, its pressure will be necessarily higher than or equal to the initial one (Abreu 1985, Pau Chang-Lu 1982, Abreu Faro and Abreu 1987, Abreu Faro and Abreu 1990). The pressure will be the same if the external force is always equal to the internal force. In this way the gas energy cannot be only a function of the volume, as can be seen in relation $U = pV/\alpha$. We can therefore introduce the entropy S variable satisfying the following conditions:

1. $U = U(S,V)$
2. $U(S_2,V_2) \geq U(S_1,V_1)$
   if $V_2 = V_1$

It is then possible to choose $S_2 > S_1$ for the situation considered in the inequality of condition 2. S_2 is equal to S_1, obviously when $U(S_2,V_2) \geq U(S_1,V_1)$ if $V_2 = V_1$. The reversible transformation is the isentropic transformation.

It is thus shown that equation $p = \alpha u$ (and the condition of tendency of equilibrium which is implicity associated with it since the piston for a given equilibrium pressure of the gas has a pressure on it higger for a compression and lower for an ex-

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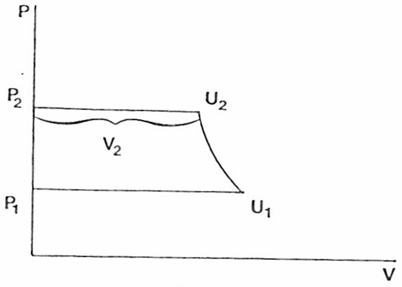
pansion) (Abreu Faro and Abreu 1987) contains the condition of irreversibility of the 2nd Principle of Thermodynamics, a strictly axiomatic formulation being therefore avoided in establishing the relations between energy and entropy.

3. GENERALIZATION OF CARNOT THEOREM

A gas constituted by interactionless particles exerts a pressure $p = \alpha u$ where a is constant and u is the energy density (Einbinder 1948).

Let us consider two reservoirs R_1 and R_2 containing the same ideal gas at pressures p_1 and p_2. The two reservoirs R_1 and R_2 have, on equilibrium points, constant physical properties per unit volume – they are sufficiently large. Also satisfy the following conditions: they may be connected by an isentropic transformation after N_2 particles of R_2 have been absorbed into the inner part of a cylinder provided with a piston, and whose volume passes from 0 to V_2. Once pressure p_1 has been attained, the volume of the cylinder goes back to zero upon injection of N_1 particles into reservoir R_1 (Fig. 1)



The efficiency of the reversible cycle which uses the ideal gas, the above-mentioned cycle, is, $\eta = 1 - \frac{T_1}{T_2}$

where T is the Kelvin Temperature, as we shall demonstrate, which generalizes the result already known for the Carnot Cycle and which can also be obtained from the latter, (from this analysis we can see why Carnot' analysis is independent of the caloric conservation hypothesis because here we have, indeed, a substance flowing between the reservoirs (Abreu 1983)).

Let U stand for the energy of the gas contained in the vessel provided with a piston and U_e denote the energy of the gas in the reservoir.

The Energy Conservation Principle permits us to write that the elementary work is

$$dW = dU + dU_e \tag{1}$$

Let us assume that the volume passes from 0 to V_i (i=1,2) reversibly in contact with R_i.
Since

$$p_i V_i = \alpha U_i$$

we have

$$p_i V_i = -\alpha U_i = U_i + \Delta U_{ei} \tag{2}$$

We therefore have

$$\Delta U_{ei} = \pm(\alpha + 1) U_i \tag{3}$$

Let us define the efficiency η:

$$\eta = \frac{|W|}{|\Delta U_{e2}|} = \frac{|\Delta U_{e2}| - |\Delta U_{e1}|}{|\Delta U_{e2}|} \tag{4}$$

or

$$\eta = 1 - \frac{U_i}{U_2} \tag{5}$$

Let us consider that both in R_1 and R_2 we have a mixture of two gases. We shall assume that one of them constituted by photons, which can pass alone from the reservoir, (H. Davy calls phoxygen to the mixture of oxygen and light) (Abreu 1993(a)).

In what concerns the particles of the other gas we consider that such a transit alone is forbiden.

Therefore for the photons we have

$$\eta_f = 1 - \frac{U_{lf}}{U_{2f}} \tag{6}$$

As to the properties of the mixture (which will henceforth be distinguished by a horizontal line) we have

$$\bar{p} = p + p_f = \alpha u + \alpha_f u_f = \bar{\alpha}\bar{u} \tag{7}$$

if we assume that the mixed gas is an ideal one; if not (7) is valid for an infinitesimal cycle (see IV and Appendix).

Since $\bar{p} = \bar{\alpha}\bar{u}$,

$$\eta = 1 - \frac{(\bar{\alpha}+1)\bar{U}_1}{(\bar{\alpha}+1)\bar{U}_2} = 1 - \frac{\bar{U}_1}{\bar{U}_2} = 1 - \frac{\bar{U}_1}{\bar{U}_2} = 1 - \frac{\bar{U}_{1f}}{U_{2f}} \quad (8)$$

since $\bar{U}_i = U_i + U_{if}$ and $\eta = 1 - \frac{|\Delta U_{ei}|}{|\Delta U_{e2}|}$

$$\bar{\eta} = 1 - \frac{|\Delta U_{ei}|}{|\Delta U_{c2}|}$$

with $|\Delta\bar{U}_{ei}| = (\alpha+1)\bar{U}_i + (\alpha_f+1)\bar{U}_{if}$ (i=1,2)

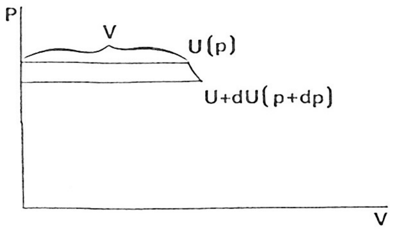
4. THE ISENTROPIC TRANSFORMATION EQUATION FROM THE GENERALIZATION OF CARNOT THEOREM

Let us consider a cycle defined as previously but assuming that pressures p_1 and p_2 differ by an infinitesimal quantity dp.

The absolute value of the work is

$$|dW| = |dp\,V|$$

where V is the volume at which the reversible expansion, without contact with the reservoir, is initiated (Fig. 2).



Since the efficiency is $\eta = 1 - \frac{U_1}{U_2} = \frac{U_2 - U_1}{U_2}$,

we have

$$\eta = \frac{|dW|}{|\Delta U_{e2}|} = \frac{dpV}{\Delta U_{e2}} = -\frac{dU}{U} \quad (9)$$

It is easy to show from (3) and (9) show that

$$UV^{\alpha} = \text{constant} \quad (10)$$

Identity (10) is the isentropic transformation equation.

5. INTRODUCTION OF THE CONCEPT OF TEMPERATURE FROM THE GENERALIZATION OF CARNOT THEOREM. THE CLASSICAL GAS EQUATION.

As previously seen, the efficiency of the cycles defined between R_1 and R_2 is

$$\eta = 1 - \frac{U_1}{U_2} = 1 - \frac{U'_1}{U'_2},$$

where U_1, U_2, U'_1 and U'_2 are two pairs of values of the gas energy contained in the cylinder when in connection with R_1 and R_2 and which define two isentropic transformation.

Since $\frac{U_1}{U_2} = \frac{U'_1}{U'_2}$, we can write

$$U = AT, \quad (11)$$

where A is constant throughout the isentropic transformations.

The efficiency can therefore be given by (9) or by

$$\eta = 1 - \frac{T_1}{T_2} \quad (12)$$

Since $p = \alpha u$ and U = AT, we have

$$pV = \alpha AT = BT \quad (13)$$

Let us assume that both R_1 and R_2 are separated by a wall, transparent only to photons, the identity (Pearson 1984) of the energy density being therefore associated with the radiation of both sides of the dividing wall. We have in both parts of R_1 (or R_2) a gas mixture of photons and another ideal gas. We admite the transparency of the dividing wall only to photons. Therefore we can have different pressures P_1 and $\hat{P}_1$ for the gas in the different sides of the reservoirs.

We have from (8)

$$\eta = 1 - \frac{U_{1f}}{U_{2f}} = 1 - \frac{U_1}{U_2} = 1 - \frac{\hat{U}_1}{\hat{U}_2} \qquad (14)$$

where Û and U are energies of N_1 particles of a gas at pressures $\hat{p}$ and p corresponding to the conditions of both sides of the dividing wall and such that it is possible to pass, by causing the volume to vary, from one condition to the other; that is, if N_1 particles from R_1 part are absorbed at pressure p_1 and energy U_1, it is possible, by varying the volume, to attain conditions N_1, $\hat{p}_1$, $\hat{U}_1$ corresponding to the other side of the dividing wall as long as contact with R_1 is maintained and therefore in the presence of R_1 radiation. An isothermal transformation of the N_1 particles has thus been defined.

From (28) and (30) we get

$$\eta = 1 - \frac{U_{1f}}{U_{2f}} = 1 - \frac{U_1}{U_2} = 1 - \frac{\hat{U}_1}{\hat{U}_2} = 1 - \frac{T_1}{T_2}$$

We have then demonstrated that the efficiency of *all* the reversible machines functioning between R_1 and R_2 is $\eta = 1 - \frac{U_{1f}}{U_{2f}}$ where U_{1f} and U_{2f} are the values of the photon gas energy on the extreme points of an isentropic transformation that connects the reservoirs.

We can then introduce the quantity temperature so that

$$\eta = 1 - \frac{T_1}{T_2}$$

THE CLASSICAL IDEAL GAS EQUATION

As we have seen, we have

$$U_i = A\,T_i$$

and

$$p_i V_i = \alpha A T_i = B T_i \qquad (16)$$

An isentropic equation is, as we have seen,

$$UV^{\alpha} = \text{cte.}$$

Since

$$U = AT,$$

we have:

$$TV^{\alpha} = \text{cte.} \qquad (17)$$

Consequently A is a function of TV^{α}

$$A = A(TV^{\alpha}) \qquad (18)$$

Since TV^{α} varies along an isothermal line, so does the A value varies along an isothermal line. Experimentally it is however found that there exist temperature and pressure ranges where A is practically constant and has the same value several gases thus satisfy pV = BT with constant B. (see Appendix).

6. THE PHOTONS ENERGY DENSITY AS A FUNCTION OF TEMPERATURE.

For the photons $\alpha_f = \frac{1}{3}$.

Taking (10) into account, we have (Einbinder 1949)

$$U_f^3 V = \text{const.} = \lambda$$

or

$$U_f^4 \frac{V}{U_f} = \lambda$$

and from (11)

$$u_f = \lambda^{-1} A^4 T^4$$

Since u_f = const. we have T = const. for R_1 or R_2 photons, therefore

$$u_f = \sigma T^4 \qquad (19)$$

where

$$\sigma = \lambda^{-1} A^4 = \text{const.}$$

for all equilibrium points and σ is a universal constant.

7. THE DEFINITION OF THE IDEAL GAS

The designation of classical ideal gas (Landsberg 1961) is used for a gas satisfying

$$pV = BT$$

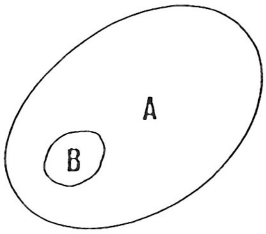
and

$$\gamma = \frac{C_p}{C_V} = \text{const.}$$

But when $U = AT$ with A being constant, with the definitions of C_p and C_V, (see Appendix) we have $\gamma = \text{const.}$ and $pV = BT$ with constant B.

Therefore, when gases satisfy $p = \alpha u$ (Einbinder 1948), a classical ideal gas is defined by $pV = BT$ with B constant. In this way, B class defined in Landsberg's (Landsberg 1961) article, coincides with A class defined in the same article for all gases satisfying $p = \alpha u$.

An ideal gas is defined by $pV = \alpha u$. It also satisfies $pV = BT$. When B has a small variation, the gas fulfils the conditions to be considered a classical ideal gas.
We may have, in short, the following scheme:



A. Ideal gas $pV = \alpha u \equiv pV = BT$
where $B = B(TV^{\alpha})$

B. If B = cte. - classical ideal gas.

8. TEMPERATURE DEFINITION THROUGH THE THERMODYNAMICS RELATION and $pV = \alpha U$.

We are now going to present the formalism that synthesis the preceding analysis.

As we seen in 2., $U = U(V,S)$.

For an infinitesimal transformation we have

$$dU = \left(\frac{\partial U}{\partial V}\right)_S dV + \left(\frac{\partial U}{\partial S}\right)_V dS \qquad (20)$$

If $dS = 0$, we have

$$dU = \left(\frac{\partial U}{\partial V}\right)_S dV \,.$$

But if (Abreu 1991) $dS = 0$,

$$dU = -p\,dV$$

since $dU = dW$ and $dW = -pdV$ in a reversible transformation (Abreu 1990, Abreu 1991).
Therefore

$$\left(\frac{\partial U}{\partial S}\right)_S = -p \qquad (21)$$

Let us make (Abreu 1985)

$$\left(\frac{\partial U}{\partial S}\right)_V = T \qquad (21)$$

We have then

$$dU = -pdV + TdS, \qquad (23)$$

in a quasi-static transformation which is not necessarily a reversible (Abreu 1990, Abreu 1991, Allis 1952, Curzon and Leff 1979)
Since $p = \alpha u$

$$p = -\frac{\partial U}{\partial V} = \alpha \frac{U}{V} \qquad (24)$$

Consequently

$$-\frac{dU}{U} = \alpha \frac{dV}{V} \qquad (25)$$

along the line S = const.
From (25) there results

$$UV^{\alpha} = \text{const.} \qquad (26)$$

along S = const.

Now from $U = U(S,V)$ and making $T = \left(\frac{\partial U}{\partial S}\right)_V$

$$\left(\frac{\partial p}{\partial S}\right)_V = + \left(\frac{\partial T}{\partial V}\right)_S \qquad (27)$$

is obtained.
Since $p = \alpha u$

$$\left(\frac{\partial p}{\partial S}\right)_V = \alpha \left(\frac{\partial U}{\partial S}\right) \frac{1}{V}$$

But since:

$$\left(\frac{\partial p}{\partial S}\right)_V = -\left(\frac{\partial T}{\partial V}\right)_S$$

$$-\left(\frac{\partial T}{\partial V}\right)_S = \alpha T \frac{1}{V} \qquad (28)$$

Along S = const. we therefore verify

$$TV^{\alpha} = \text{const.} \tag{29}$$

Since $UV^{\alpha} = \text{const.}$ is also verified along S = const. then

$$U = AT \tag{30}$$

CONCLUSIONS

It has been the aim of this article to show that from equation $pV = \alpha U$ for an ideal gas, it is possible to establish the concept of temperature. For this purpose we have used two sufficiently large reservoirs where, on equilibrium points, the physical properties per unit volume are constant. Alternatively and in an equivalent way, such a concept can be established through $p = \alpha u$ and the relation $T = \left(\frac{\partial U}{\partial S}\right)_V$ (Abreu 1985). To this end, it is demonstrated that the efficiency of a cycle described by a gas satisfying $p = \alpha u$ is $\eta = 1 - \frac{U_1}{U_2} = \text{cte.}$ where U_1 and U_2 are the gas energies on the extreme of isentropic transformations that connect both reservoirs or, in a more abstract way, through the formalism emerging from $U = U(S,V)$ since the entropy arises as a consequence of the irreversibility inerent in $p = \alpha u$ (Abreu 1985), and of the equilibrium implicity assumed (Abreu Faro 1987). Since light satisfies $p = \alpha u$ the efficiency of all cycles is

$$\eta = 1 - \frac{U_{1f}}{U_{2f}} = 1 - \frac{T_1}{T_2}$$

It is demonstrated that equation $pV = BT$ is satisfied for all ideal gases. The classical ideal gas is defined only through the condition $B = \text{const.}$ and not through both conditions $pV = BT$ where B is constant and $\gamma = \frac{C_p}{C_V} = \text{const.}$ (Landsberg 1961, Landsberg 1974).

A great simplicity is, in this way, achieved and tautologies (Miller 1960, Landsberg 1961, Pearson 1984, Fermi 1936, Buchdahl 1973, Home 1977, Ehrlich 1981, Thomsen 1983) are avoided, a generalization of Carnot theorem having been resorted to, which, together with the Energy Conservation Principle, clearly shows the non-essential character of the First Principle of Thermodynamics (Abreu 1990, Abreu 1991, Abreu 1993(b), Abreu 1994). This being so one can understood and reinterpret the historical way of introducing the physical ideas of thermodynamics with a new perspective emerging from the generalization of Lord Kelvin postulate: A transformation whose only final result is to transform internal energy into Work is impossible (Abreu 1991).

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APPENDIX

Definition and computation of $\bar{\gamma}$
From H = U + pV
we have

$$H = U + \alpha U = (\alpha + 1)U$$

Since $p = \alpha u$.
Therefore

$$\left(\frac{\partial H}{\partial T}\right)_V = (\alpha + 1)\left(\frac{\partial U}{\partial T}\right)_V ;$$

or

$\left(\frac{\partial H}{\partial T}\right)_V = (\alpha + 1)\ C_V$. Only for an classical ideal gas we have $\left(\frac{\partial H}{\partial T}\right)_V = \left(\frac{\partial H}{\partial T}\right)_p = C_p$.

Since

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V .$$

Defining

$$\gamma = \frac{\left(\frac{\partial H}{\partial T}\right)_V}{\left(\frac{\partial U}{\partial T}\right)_V},$$

we have

$$\gamma = (\alpha + 1)$$

Then, an isentropic equation is

$pV^{\gamma} = cte.$

Consider a mixture of an classical ideal gas + photons.

The $\bar{\gamma}$ mixture can be calculated from

$$\bar{H} = \bar{U} + \bar{p}V$$

$$= U + U_F + NKT + \frac{1}{3}aT^4V$$

$$\bar{H} = NKT\frac{5}{2} + \frac{4}{3}aT^4V$$

and from the internal energy in

$$\bar{U} = \frac{3}{2}NKT + aT^4V$$

Therefore $\bar{\gamma}$ for the mixture is

$$\bar{\gamma} = \frac{NK\frac{5}{2} + \frac{4}{3}a4T^3V}{NK\frac{3}{2} + 4\ aT^3V} \qquad \text{(A)}$$

The mixtures value of $\bar{\gamma}$ varies from 1.33 (photon γ) to 1.66 (classical monoatonic γ). Since $TV^{(\bar{\gamma}-1)} = $ constant we can define the isentropic equation by an interactive method. This being so, with generality, when a classical ideal gas is compressed reversibly $\bar{\gamma}$ change, satisfying $TV^{(\bar{\gamma}-1)}$constant and (A). The mixture, of course satisfies the equation

$$\bar{p}\bar{V} = (\bar{\gamma} - 1)U$$

$$\bar{p}\bar{V} = (\bar{\gamma} - 1)\left(\frac{3}{2}NKT + aT^3V\right)T$$

$$\bar{p}\bar{V} = BT$$

With

$$B = (\bar{\gamma} - 1)\left(\frac{3}{2}NKT + aT^3V\right)$$

Therefore for a gas without interactions, B value change because the gas is not a classical or (and) because the photon gas can not be neglected.