AN INVESTIGATION OF THE SECOND LAW OF THERMODYNAMICS

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PREFACE

The feasibility of a self-actuating refrigerating machine, that is, "the perpetual motion of the second kind," has ceased to be a question universally identified as "*absurd,*" "*necessarily impossible,*" "*an indication of ignorance,*" et cetera. Furthermore, throughout the scientific world, at the present time, a rapidly increasing multitude is becoming seriously interested in the outcome of this question and an early *positive* settlement will afford general satisfaction.

This brief contribution to the science of thermodynamics is an investigation pursued along the strictest lines of philosophy and reasoning with the view of determining what particular positive knowledge is now lacking and must be acquired in order positively to settle this question.

The investigation discloses that all knowledge involved is known positively, excepting exact determination of the value or measure of the variations of the "disgregation of expansion" and the two kinds of "specific heat" which result by reason of changes in physical state as determined by changed conditions of pressure, density, and temperature. However, positive knowledge pertaining to this relation, although somewhat meager and obtained from sporadic experimentation, is vouched for by some of the most eminent investigators of the present day, and indicates that "perpetual motion of the second kind" is feasible.

The matter of co-ordinating these six manifestations as functional variables, instead of only the usual three, constitutes a much-needed reform in the science of thermodynamics, and consequently means a more complex science. However, since Nature is not simple but is infinitely complex, all advancement in science necessarily means progression from simple crudeness to complex refinement.

Therefore, this paper is further purposed as a plea for experimental research to establish extended positive knowledge regarding this functional relation; and thereby indirectly settle the question at issue, positively and finally.

To savants with desire to pursue this subject further and in different manner, the author would mention several of his papers which were read at the meetings of the American Association for the Advancement of Science, beginning in the year 1903, and are available from the reference shelves of: the National Library of Congress, Washington, D.C.; the Library of the Franklin Institute, Philadelphia; the Astor-Tilden-Lennox Library, New York City; the Crerar Library, Chicago; also, some communications published in *The Engineer* (London): see issues of June 21, 1912, p. 658; July 26, 1912, p. 90; September 6, 1912, p. 259.

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THE SECOND LAW OF THERMODYNAMICS

The "principle of cause and effect" is our fundamental analytical comprehension of a happening, and consequently is our fundamental analytical criterion for "Fact." This principle means that cause and effect are true equivalents.

Phenomena constitute the only source from which positive knowledge is derived; consequently, as relates to physical science, all truly established facts or principles must be derived, either directly or indirectly, from manifestations of Nature revealed either directly or by the aid of experimentation. Consequently, as relates to physical science, a postulation necessarily imposes on Nature an exacting requirement which must be upheld by the physical properties of matter in order to uphold the postulation as a truth.

Indirect derivation is properly effected by co-ordinating a plurality of more directly derived facts. However, it must ever be kept in mind that the scope of an indirectly derived fact or principle cannot be considered as established beyond the limitations imposed by the established facts comprised in the particular co-ordination from which it is derived. Each co-ordinated fact necessarily contributes its quota to the formulation of the resultant derived fact or principle, and such distinct contribution is properly identified as the significance of that particular contributing fact; furthermore, this means that the significance of a fact or principle is not necessarily a fixed contribution for all co-ordinations, but is dependent upon the other facts or principles which are comprised in the particular co-ordination considered.

It will be perceived that when a postulation is comprised in the co-ordination, a positive fact or principle cannot be derived therefrom, but necessarily a *derived postulation* results. Also, subsequent discovery of additional pertinent facts or principles which should have been included in the co-ordination necessarily relegates the principle which was derived from such incomplete source to its proper limitations as hereinbefore described, and necessitates the derivation of a new principle which must be in accord with a revised co-ordination.

Since advancement in science eventually discloses new facts and principles which are pertinent and should have been included in the co-ordination from which accepted principles were derived, it necessarily results that promulgation of a principle as a generalization devoid of limitations is naturally abhorrent to all scientists possessed of true acumen.

From what precedes, it will be perceived that in order to investigate the truth of a principle and locate an underlying falsity if it exists, when direct verification by experimentation is inexpedient, it becomes necessary:

First: To determine what positively known facts or principles are pertinent in the matter.

Second: To determine if the principle results from a co-ordination of a complete list of such facts, or only from a partial list of same, or only from a list in which postulation is involved.

Third: To determine what requirement is imposed by postulation, and to determine if it is upheld by the properties of matter involved; and further to determine to what extent or limitations the properties of matter can uphold such postulation.

The science of thermodynamics, in its present-day state, is founded on two fundamental underlying principles; one is an axiom, the other is a bald postulation.

The "first" fundamental underlying principle or law is commonly known as the "first law of thermodynamics," and is merely a specific formulation of that which in a more generic formulation is known as "the principle of conservation of energy," which again in a more generic formulation is known as "Newton's principle of action and reaction," which again in a more generic formulation is known as the "principle of equivalence in cause and effect." Since, as was hereinbefore explained, the generic formulation of this principle is our fundamental analytical criterion for "Fact," necessarily it is truly an axiom.

The "second" fundamental underlying principle is simply the *denial* of the so-called chimera known as "the perpetual motion of the second kind." In the following simple manner, Carnot demonstrated that this "denial" necessarily is the resultant of the co-ordination of "the principle of conservation of energy," with "the *materialistic* theory of heat":

> "An unlimited creation of motive power, *without consumption* either of caloric or of any other agent whatever, constitutes perpetual motion. Such a creation is entirely contrary to ideas now accepted, to the laws of mechanics and of sound physics. It is inadmissible."

As a mere philosopheme, it may here be remarked that, since this demonstration shows in what manner this "denial" is accurately derived from a co-ordination of two principles, destruction of one of these principles necessarily means destruction of the derived principle. Consequently, the replacement of the theory of indestructible material heat by the conversional theory necessarily causes this "denial" to become untenable.

Carnot subsequently arrived at this same conclusion, and is explained farther on.

Also, it may here be mentioned as an interesting fact that the late Henri Poincaré, throughout his writings, frequently expressed dissatisfaction with the "second law," and in one instance as follows:

> "The second law of thermodynamics does not seem to be compatible with the first law."

It seems that the manner by which he arrived at this conclusion has never been disclosed.

In a manner which does not involve the nature of heat, Carnot showed that a cyclic acting machine to effect "perpetual motion of the second kind" means a combination of a heat motor with a heat pump, in which the thermodynamic agent of the motor must be more efficient than that of the pump, by an amount sufficient to overcome the mechanical inefficiencies of the entire apparatus, in addition to the useful work derived; and that, when the apparatus is assumed to operate in a perfect manner, that is, free from all manner of irreversibleness, *the assumption of inoperativeness necessarily imposes the following principle:*

> "The motive power of heat is independent of the agents employed to realize it; its quantity is fixed *solely* by the temperature of the bodies between which is effected, finally, the transfer of the caloric."

This is Carnot's formulation of what is now known as the "second law of thermodynamics," and has never been improved upon by the many ambitious writers who are identified with its various formulations extant. It will be perceived that, although the derivation of the second-kind perpetual motion "denial" involves the nature of heat, this so-called "second law" is derived from this "denial" in a manner which does not further involve a consideration of the nature of heat and consequently agrees with the present-day state of the science. Furthermore, it will be perceived that it is not a formulation of a negation, neither is it verbose, but concisely formulates the limitations which apply to the possibilities of a heat engine, as determined by *accepting* this "denial" and co-ordinating same with "the principle of conservation of energy."

Also, *in a manner which does not involve the nature of heat*, Carnot followed this matter up and demonstrated that the specific manifestation of Nature which this "second law" imposes is that, in a reversible cycle in which the applied heat is transferred at one temperature and the discharge of heat is effected at one other temperature, *the average rate of conversion of a given quantity of applied heat must be the same for all agents, for the same range of temperature;* and, furthermore, that this requirement must hold true for *all* ranges of pressure, or of density, in which the cycle may be operated. It results as a mathematical deduction from this principle that the efficiency function, that is, Carnot's function, must be the same for *all* substances at the same temperature. Since the manner of deducing this principle from the "second law" does not involve the nature of heat, it necessarily agrees with the present-day state of the science, and is the *crux* which has never been satisfactorily upheld, either directly or indirectly, by reliable knowledge derived from experimentation.

Rate of conversion means: "Amount of external work produced by a unit of temperature-drop"; and as applies to such reversible cyclic conversion, it is commonly known as "the thermodynamic function"; and when this function corresponds to a *unit* measure of applied heat, it is known as "Carnot's function."

However, Carnot subsequently repudiated the materialistic theory of heat, the second-kind perpetual motion "denial" which he had derived from same, the so-called "second law" which he had derived from this "denial," and necessarily all of the principles which he had derived from this "second law," unequivocally, and by the following precise statement:

> "When a hypothesis no longer suffices to explain phenomena, it should be abandoned. This is the case with the hypothesis which regards caloric as matter, as a subtle fluid. . . . . But it would be difficult to explain why, in the development of motive power by heat, a cold body is necessary; why, in consuming the heat of a warm body, motion cannot be produced."

Thus, in this brief observation in regard to a cold body, Carnot not only states that it would be difficult to explain why "perpetual motion of the second kind" is not possible, but at the same time he explains what it means.

Also, in this manner, he has certainly established his identity as the original pioneer in the movement to eliminate the pernicious falsity which at the present time underlies the entire science.

In order to explain this seeming anomaly, it may here be proper briefly to repeat some history which has already been published elsewhere, and explain that:

"A sparse edition of Carnot's now famous treatise on the *Motive Power of Heat* was published in the year 1824, that he died suddenly in the year 1832. However, in the intervening time, by reason of his changed belief regarding the nature of heat, he recorded some notes and memoranda apparently with the view to publishing a revised treatise and also to prosecute some important experimentations. Fortunately, his original manuscript of these notes and also of his published treatise were preserved in the archives of the French Academy of Science where they remained in oblivion until the year 1878 when they were published in their entirety."

His aforementioned repudiation of the "second law," and also his formulation of what is now known as the "Joule-Mayer principle of conservation of energy" were comprised in these notes.

Professors Rudolph Clausius and William Thomson (Lord Kelvin) were chiefly responsible for the present-day deplorable state of the particular branch of the science of thermodynamics which relates to the motive power of heat, particularly regarding the "second law" question. Both had acquired preponderant reputation as mathematicians, and respectively announced that they had established the "second law" as true by reconciling experimentally derived facts with mathematical deduction. This announcement from such eminent source, unfortunately, seems to have diverted censorial scrutiny, and was swallowed as gospel truth by almost the entire scientific world.

Clausius arrived at this conclusion by properly assuming that, sufficient for all mundane affairs, some one of the so-called permanent gases is amenable to the "Boyle-Gay Lussac law," and that consequently the location of a so-called absolute-zero on a perfect-gas thermometer is accurately expressed by the reciprocal of such fluid's "coefficient of expansion." Upon this assumption he accurately deduced that, for such fluid, the rate of reversible cyclic conversion of a given quantity of applied transferred heat is necessarily a measure or value which is expressed by ratioing the quantity of this transferred heat by the so-called absolute-temperature at which it is transferred. Furthermore, he showed that, *in order to uphold the "second law," it becomes necessary that this formulation must also hold true for all substances.*

Transferred heat, ratioed by so-called absolute-temperature corresponding to such transfer, is a mathematical conception which he calls "entropy"; and from the principle just enunciated, he accurately derived the following principle:

> "The second law means that, in a reversible cycle, the aggregate of positive entropy *must* be equal to the aggregate of negative entropy."

In that manner, Clausius accurately brought the question to the following simple positive issue having but one alternative:

> Either abandon the "second law"; or abandon experimentally derived values for "disgregation of expansion," and the two kinds of "specific-heat," when a co-ordination of same to determine the rate of reversible cyclic conversion does not uphold "entropy" as the true measure of such rate, for all regions of pressure, density, and temperature, and also for all substances.

When Clausius brought the question to this abrupt conclusion, Kelvin had expended much effort during several years in formulating efficiency tables for steam and other heat engines, based on the experimentations of Regnault and other investigators.

These tables cover merely a meager range of pressure, but nevertheless disclose a very considerable discrepancy from the requirement imposed by the Clausius ultimatum. However, Kelvin finally recognized the alternative nature to which the question had been accurately brought, and concluded that such discrepancies necessarily *must* be attributed to inaccuracies of experimentation. Both, it would seem by mutual assent, then abandoned further consideration and discussion of the experimental phase of the question, and adopted the *postulated* "second law" as the true alternative.

This certainly does not appear to be a very strict reconciliation of postulation with experimentation, and possibly each foresaw in such procedure an easy road to much fame: for one, the announcement to the scientific world of a finite absolute-zero on Nature's scale of temperature; for the other, the announcement that "the entropy of the Universe tends toward a maximum," and the consequent significance regarding ultimate death of Nature.

Kelvin's absolute-zero doctrine has already been destroyed by reason of advancement in the art of refrigeration whereby liquefaction of the so-called permanent gases became a reality, coordinated with the fact that "specific-heat decreases rapidly with increased cold."

Also, already, present-day reliable determinations for "specific heat" and "disgregation of expansion," as derived from experimentations by eminent investigators, disclose reliable facts which cannot be reconciled with the aforementioned deductions which Clausius accurately derived from the "second law."

THE NEW THERMODYNAMICS

AN ADDENDUM TO PAPER HAVING THE TITLE:
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LAW OF THERMODYNAMICS"

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THE NEW THERMODYNAMICS

The principal purpose of this brief contribution to the science of thermodynamics is to present a simple and positive mathematical refutation of the "second law," and incidentally to determine what particular peculiarities must be possessed by a substance in order that it can be amenable to the Clausius formulation for efficiency. Another purpose is to present what seems to be a simple and desirable foundation upon which to rebuild the entire science of "motive power of heat."

"Specific heat," reckoned as variable instead of as constant, is the particular fundamental feature which is peculiar to this new departure, and consequently introduces a further rate of change or additional differentiation into the mathematics of the science.

Furthermore, postulation is taboo. Consequently, by reason of the fact that "specific heat" is *always* a variable function to a greater or less degree for all substances, the conception of a finite thermometric location for absolute zero of temperature will not be tolerated. Therefore, "temperature" must be reckoned in the relative sense. However, volume and pressure may be reckoned in the absolute sense.

The necessity of holding to this qualification becomes apparent from a consideration of the fact that the idea of "absolute temperature," as commonly conceived at the present day, was derived from a mathematical conception which is functionally affected by variation of "specific heat."

It does not seem necessary to explain why an investigation of the "motive power of heat," for the purpose of this particular research, simply reduces to a study of the efficiency of a Carnot cycle.

It is purposed to refute the "second law" by an accurate and systematic mathematical determination of the theoretical efficiency which is obtainable from various kinds and conditions of working media, when operating in a Carnot cycle which is identically the same for all in regard to extent of temperature range and also in regard to the temperature location of such range, but without any other restrictions. Therefore, this manner of procedure enables a comparison of such results to show that: For the same range of temperature, "possible maximum efficiency" is *not* the same for all kinds and conditions of working media, and consequently constitutes a positive refutation of the "second law," by refuting a so-called principle which is supposed to uphold the "second law" in a manner that is understood by all students of thermodynamics.

Applying the calculus of ratios or rates, as conceived by Newton and Leibnitz, and keeping in mind the usual pressure-volume diagram of a Carnot cycle in which the vertical ordinates represent pressure and the horizontal ordinates represent volume, it is perceived that such diagram by means of a series of vertical lines may be subdivided into differentiations of volume, and in like manner by means of horizontal lines may be subdivided into differentiations of pressure.

This manner of differentiating means that, throughout this mathematical treatment of the subject, $\frac{dp}{dt}$ represents the rate of change of pressure condition corresponding to unchanged volume, and $\frac{dv}{dt}$ in like manner represents the rate of change of volume condition corresponding to unchanged pressure. Therefore, the fundamental formulation from which to derive the evaluation for the external work of the entire cycle may be written:

$$d^2W = dp \times dv, \qquad (1)$$

in which W represents the external work produced by the entire cycle.

Consequently, the derived integral equation which represents the evaluation of the external work produced by the entire cycle may be formulated thus:

$$W = H_2 - H_1 = \int_{t_1}^{t_2} \int_{\text{Compression adiabatic}}^{\text{Expansion adiabatic}} dp \times dv \qquad (2)$$

in which t_2 represents the temperature at which the applied heat H_2 is transferred to the medium, and t_1 represents the lesser temperature at which the medium discharges the heat H_1.

The "*rate*" of such cyclic conversion, *with respect to temperature drop*, necessarily means the portion of such diagrammatic area which represents an imaginary Carnot cycle comprised between the same adiabatic limits but corresponding to a unit of temperature drop. Consequently, the work produced by the entire cycle represents the aggregate or summation of a succession of such smaller cycles which respectively correspond to each unit of the temperature drop of the entire cycle, and each intermediate cycle comprised in such series is supposed to receive its supply of applied transferred heat from the one which next precedes, and to transfer its discharged heat into the one which next follows. This conception originated from Carnot.

The next procedure is to derive from equation (2) the evaluation of the work which is represented by one of these *rate cycles* located at any representative temperature t.

By differentiating equation (2) with respect to temperature, there results:

$$\left(\frac{dW}{dt}\right)dt = \int_{\text{Compression adiabatic.}}^{\text{Expansion adiabatic}} dp \times dv \qquad (3)$$

By ratioing equation (3) in a manner which is equivalent to an integration for temperature limits which correspond to a range of temperature restricted to a unit measure of extent, there results:

$$\left(\frac{dW}{dt}\right)\frac{dt}{dt} = \frac{dW}{dt} = \phi = \int_{\text{Compression adiabatic}}^{\text{Expansion adiabatic}} \left(\frac{dp}{dt}\right) \times dv \qquad (4a)$$

$$= \int_{\text{Compression adiabatic}}^{\text{Expansion adiabatic}} \left(\frac{dv}{dt}\right) \times dp \qquad (4b)$$

which is the basic formulation for *rate* of cyclic conversion with regard to temperature drop, *as applies to a Carnot cycle.* This particular evaluation is commonly known as "the thermodynamic function" and is usually designated by the symbol ϕ, or sometimes $(\phi a - \phi b)$; and when the limitations for the cyclic limiting adiabatics are restricted so as to correspond to an *initial* application of a *unit* of transferred heat, it is known as "the efficiency function," that is, "Carnot's function."

However, this form of the evaluation is not well adapted to practical use, and therefore it becomes desirable that the ratio $\frac{dp}{dt}$, which is an expression that represents "*constant volume change of pressure*" corresponding to a unit change of temperature, shall be expressed by $\left(p\times\left[\frac{P}{C}\right]\right)$, in which $\left[\frac{P}{C}\right]$ is the symbol for the "coefficient of pressure change," that is, a factor which is always a function of temperature, and sometimes also a function of pressure or of volume, and which, when multiplied by the corresponding pressure, results in a product that represents such particular pressure change. Also, in like manner it becomes desirable that the ratio $\frac{dv}{dt}$, which is an expression that represents "*constant pressure change of volume*" corresponding to a unit change of temperature, shall be expressed by $\left(v\times\left[\frac{V}{C}\right]\right)$, in which $\left[\frac{V}{C}\right]$ is the symbol for the "coefficient of volume change," that is, a factor which is always a function of temperature, and sometimes also a function of volume or of pressure, and which, when multiplied by the corresponding volume, results in a product that represents such particular volume change; furthermore, it may be explained that this particular coefficient is a conception which is not new to the science, and is known as the coefficient of expansion.

Therefore, by substitution of these expressions, equations (4*a*) and (4*b*) become:

$$\frac{dW}{dt}=\phi=\int_{\text{Compression adiabatic}}^{\text{Expansion adiabatic}}\left(p\times\left[\frac{P}{C}\right]\right)\times dv \tag{5a}$$

$$=\int_{\text{Compression adiabatic}}^{\text{Expansion adiabatic}}\left(v\times\left[\frac{V}{C}\right]\right)\times dp \tag{5b}$$

in which p and v apply only to the involved representative isothermal line; also $\left[\frac{P}{C}\right]$ and $\left[\frac{V}{C}\right]$ respectively may be a function of t, p, and v.

Since "specific heat" is a concept which means: quantity of heat required to effect a unit change of te nperature to a unit of mass, necessarily it results that,

$$p \times \left[\frac{P}{C}\right] = M \times \frac{f(Kv)}{v},$$

and in like manner

$$v \times \left[\frac{V}{C}\right] = M \times \frac{f(Kp)}{p},$$

in which (Kv) represents "specific heat for constant volume," (Kp) represents "specific heat for constant pressure," and M represents the mass of the working fluid and is a constant measure or value. Therefore, by substituting these expressions, equations (5*a*) and (5*b*) become:

$$\frac{dW}{dt} = \phi = M \times \int_{\text{Compression adiabatic}}^{\text{Expansion adiabatic}} \frac{f(Kv)}{v} \times dv \qquad (6a)$$

$$= M \times \int_{\text{Compression adiabatic}}^{\text{Expansion adiabatic}} \frac{f(Kp)}{p} \times dp \qquad (6b)$$

in which v and p apply *only* to the involved representative isothermal line; also (Kv) and (Kp) respectively may be a function of t, p, and v.

These four equations (5*a*), (5*b*), (6*a*), and (6*b*) necessarily are fundamental or generic formulations. Furthermore, equations (6*a*) and (6*b*) are particularly interesting because they disclose the subtle significance of "specific heat," as it affects cyclic efficiency, which is a matter that was not known or properly understood in the prior state of the science.

Having thus formulated the *true generalization* for "rate" of Carnot cyclic conversion, it becomes proper to continue the mathematics from this stage merely as a matter of progressive specialization from generic to specific, in successive steps corresponding respectively to the evolution of an involved variable into a constant, and thereby at each of such stages separate for further specialization toward the ultimate goal of physical constants as exemplified by a "*perfect gas*," certain corresponding groups of substances as determined by experimentally derived knowledge regarding their physical properties.

From the viewpoint of pure mathematics, each of these successive eliminating stages constitutes a refutation of the claim that the formulation finally derived in such manner and applicable only to a "*perfect gas*" is a true generalization, that is, holds true for all kinds and conditions of matter. This, in itself, is sufficient to end the investigation, then, and there. However, it is purposed to progress the classification to the ultimate limit of specialization, and compare with same the experimentally measured evaluations for "rate of conversion" corresponding to some *saturated vapor* which has been investigated experimentally, is typical for all saturated vapors, and *plainly* shows the typical characteristics; and thereby disclose discrepancies which are imposed by Nature and cannot be questioned.

Therefore, the next procedure is to derive from equation (5*a*) a less generic formulation which will apply *only* to a substance which maintains a constant value for $\left[\frac{P}{C}\right]$ during the entire change of volume at constant temperature t between the limiting adiabatics. Consequently, such derived equation necessarily will hold true for the "saturated vapor" type of Carnot cycle, also for the Carnot cycle of a "perfect gas," but will not hold true for an "imperfect gas." Consequently, this particular step of gradation causes equation (5*a*) to become:

$$\frac{dW}{dt}=\phi_1=\left[\frac{P}{C}\right]\times\int_{\text{Compression adiabatic}}^{\text{Expansion adiabatic}} p\times dv \qquad (7)$$

in which p applies only to the involved representative isothermal line; and $\left[\frac{P}{C}\right]$ is a function of temperature *only*, but not necessarily a constant function, nor necessarily the same value for all substances.

The next procedure is to derive from this equation (7) a formulation which again is less generic, and will apply *only* to a "perfect gas." In such case, the Boyle-Gay Lussac law imposes the feature that "specific heat" is constant for all conditions of state; consequently all locations on an isothermal line necessarily correspond to a condition of unchanged "intrinsic energy," which means absence of proclivity to divert applied heat into so-called "latent energy"; therefore, necessarily $\int p \times dv$ *now* represents the equivalent of the applied transferred heat and is conceived to be received at constant temperature and from the next preceding cycle and is symbolized as h. Therefore, by substituting this expression, equation (7) becomes:

$$\frac{dW}{dt} = \phi_2 = \left[\frac{P}{C}\right] \times h, \qquad (8a)$$

in which $\left[\frac{P}{C}\right]$ is not a constant, but must be evaluated for the particular isothermal involved. However, the Boyle-Gay Lussac law also imposes the additional feature that:

$$\left[\frac{P}{C}\right] \times p \times v = \text{Constant}.$$

Furthermore, by reason of acceptance of Dalton's law, it is believed that this particular constant is common to *all "perfect gases"* having a common value for $p \times v$ at a common temperature, and may be derived from *any one* of such by simple experimentation; nevertheless, this particular Dalton principle, as a generalization without limitations, is somewhat questionable; however, this question does not affect this investigation.

Also, for a "perfect gas" $\left[\frac{P}{C}\right]$ necessarily has the same evaluation as $\left[\frac{V}{C}\right]$. Consequently, equation (8a) may be written:

$$\frac{dW}{dt} = \phi_2 = \left[\frac{V}{C}\right] \times h. \qquad (8b)$$

It is important to note that equation (7) marks the particular stage in the process of successive derivation from the generic to the specific, where parting of the ways occurs for the "saturated vapor" type of cycle, and the "perfect gas" type. This matter will be commented upon farther on.

This equation (8*b*) is the famous formulation which Clausius accurately arrived at by a different method of procedure. His purpose was to arrive at a *formulation* which would hold true for a "perfect gas." He was not interested in deductions of a more generic nature because he did not intend to *question* the "second law"; and he accurately perceived that *acceptance of that law necessarily means that an accurately derived formulation of the "thermodynamic function" for any substance must also hold true for all substances*, and that a "perfect gas" is the simplest thermodynamic medium from a mathematical point of view and consequently the most convenient to investigate.

Also, Kelvin was not eager to *question* the "second law," but attempted to evaluate "the thermodynamic function" in *tabulated form derived from known properties of steam.* However, he finally accepted the Clausius argument, and abandoned his experimentally derived tables *because they showed a very considerable discrepancy* in comparison with evaluations derived by the Clausius method which does not necessitate any experimentation other than *one* determination for "coefficient of expansion" for some *one* "perfect gas."

Referring to equation (7), and relating to working media which are adapted for use in the "saturated vapor" type of cycle and are amendable to this equation, Nature has *not* imposed a value for $\left[\frac{P}{C}\right]$ which will compensate for the vagaries of disgregation and uphold a common "efficiency function," and thereby refutes the "second law."

Furthermore, all of such kind of substances differ from a "perfect gas" in a manner which is manifested by a difference in the evaluation of $\left[\frac{P}{C}\right]\times p\times v$; and since this expression is a constant for the "perfect gas," and is variable for these other substances, it results that their respective evaluations for ϕ will depart from the "perfect gas" ϕ to an extent which is a function of pressure. This necessarily constitutes an additional refutation of the "second law."

Relating to the "saturated vapor" type of Carnot cycle, the

Clausius conception of entropy is a true measure of the initial $\frac{dW}{dt}$ only for a particular temperature having a scale location which is different for different substances; whereas, at other temperatures, the amount of deviation from the true measure is dependent upon the extent of departure from such fixed location; furthermore, the nature of such deviation, in a positive and negative sense, is dependent upon the *direction* in a positive and negative sense of such departure on the temperature scale.

It may be remarked that the *rate* of such deviation from the entropy conception is not the same for all substances.

The following tabulation shows this matter plainly, and was derived from recently published tables (Goodenough's) for saturated ammonia (NH_3) which are believed to be a reliable exposition of experimentation for $\frac{dp}{dt}$, "specific volume of vapor," and "specific volume of liquid." However, in deriving the values for "latent heat of evaporation," the pernicious practice of dispensing with experimentation and co-ordinating the second law of thermodynamics with these experimentally derived variables was adopted in order that such tables would be compatible with the so-called thermodynamic laws; consequently, Goodenough's tabulated values for "latent heat of evaporation" are rejected for use in this investigation, and the Dieterici curve is accepted as a substitute because it agrees quite nearly with experimentally derived values:

At -40	degrees	Fahr.,	deviation	from	entropy	$=-15$	per	cent
" $+70$	"	"	"	"	"	$=0$	"	"
" $+160$	"	"	"	"	"	$=+9\frac{8}{10}$	"	"
" $+273.2$	"	" critical point						

In conclusion, it may be remarked that thorough experimentation, carried into extreme regions of pressure and density, will contribute much to advance the science of motive power of heat and the art of mechanical refrigeration.