

# A COMMENTARY ON THE FIRST LAW OF THERMODYNAMICS

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## Introduction

Quantitative description of physical and chemical processes non-mechanical in character yet presenting a mechanical side has been greatly extended and generalized by applying to these processes the method employed for the description of purely mechanical changes of state. In mechanics the method consists in measuring a change of the "energy" of a body by the work requisite to alter the level, or the velocity of motion, or the state of strain of the body, and then describing any given mechanical process by formulating the interconversion of the potential and kinetic energies of a body acquiring or losing motion, or by formulating the transfers of mechanical energy that occur between different bodies.

Many processes not purely mechanical in character can be brought into connection with mechanical operations. Processes of this sort are almost coextensive with the range of physics and chemistry. Fusion and evaporation, electric and magnetic attraction, electrolysis, combustion, and radiation, can all be associated with absorption or development of work. The connection may be to some extent indirect, in that the process alters the temperature of an extraneous body or effects some change of state that can be replaced by a change of temperature. If the temperature of a body is raised, the action of the process is that of a development of work expended in overcoming friction; if the temperature of a body is lowered, the action is that of an absorption of work so expended. In any event a change of state of the type in question can be understood to consist of an absorption or development of work, effected either directly, or else through intervention of an operation equivalent to a change of the temperature of another body, or in both of these ways at once.

Changes of state of this type are "thermodynamic" processes. When the "energy" of a body undergoing a thermodynamic change of state is defined to be a quantity whose change of value is equal to the quantity of work directly and indirectly absorbed by the body, and it can be shown that this quantity of work depends only on the end states of the body, a quantitative description of the thermodynamic process is achieved by a formulation of the transfers of energy that occur between the bodies participating in the operation.

The quantity of work directly and indirectly absorbed by a body undergoing a thermodynamic change of state is in fact determined by the end states of the body. To exhibit the reasoning by means of which this conclusion is reached, for the class of thermodynamic changes consisting of processes involving compression, expansion, change of temperature, fusion, evaporation, the formation of homogeneous mixtures, and changes of chemical state, is the purpose of the present discussion. The form of the argument is intended to make clear, for a limited class of operations, the actual content of the first law of thermodynamics. Analytical formulations of the law are not considered. They form, properly, a matter for independent examination.

### **Changes of state of bodies**

At the outset it must be clearly understood what is to be meant by certain terms, by a "body," a "change of state," the "path" of a change of state, a "supplementary" change of state, and a "work-development."

Any given material object or assemblage of objects, as long as no portion of it is removed and no extraneous matter is added to it, shall be termed a given "body." A mass of air or of gunpowder, a block of metal, a quantity of brine together with an overlying layer of water vapor, and a closed receptacle together with its contents, are bodies. During the process of heating coexistent brine and vapor contained in a rigid shell, the layer of brine is not a body, for a portion of this object is removed in the evaporation that ensues.

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Any body may be brought from any quiescent state to a new quiescent state by effecting a change of its level or its form, by altering its volume or its temperature, by electrifying it or magnetizing it, or by causing it to undergo a chemical change, and the like. When a body has been brought from one quiescent state to another, it shall be said to have undergone a "change of state." And this change shall be considered to be the same change of state, whatever the manner in which the process has occurred. Thus a block of metal may be slowly or rapidly lowered from one position to another, in each case undergoing the same change of state. Again, a given mass of air may be brought from the volume  $V_1$  at the temperature  $\tau_1$  to the greater volume  $V_2$  at the higher temperature  $\tau_2$ , by raising its temperature to  $\tau_2$  at constant volume, and then isothermally expanding until the volume becomes  $V_2$ ; or by isothermally increasing the volume to  $V_2$ , and then raising the temperature to  $\tau_2$  at constant volume; or by bringing the volume and temperature of the mass to their new values in any relatively abrupt way. In any of these cases the body undergoes the same change of state, namely the change from the state  $V_1, \tau_1$  to the state  $V_2, \tau_2$ . When a change of the state of a body is effected in different ways, it shall be said that the "path" of the change of state is different in the different cases.

By the "state" of a body shall always be understood a quiescent state. The meaning of the term "state" shall not be broadened to include a "steady state," as that of a body rotating about an axis under the action of constant forces, or a "turbulent state," as that of an exploding mass of gunpowder, or as that of a mass of water in which currents are moving and differences of temperature exist.

#### Supplementary changes of state

It is important to observe that every *actual* change of state is a *spontaneously occurring* change of the state of the assemblage of all the bodies that participate in the process.

Consider an illustration. Under an exhausted receiver,

a vertical cylinder contains a block of metal and an overlying mass of air confined by a heavy piston working without friction. When the isolated system under the receiver is in a state of rest, and has in consequence a uniform temperature, the block of metal is instantaneously replaced by another block, of the same dimensions but having a higher temperature. A change of state of the system ensues. The block contracts and its temperature falls; the air expands and its temperature rises; the cylinder and piston become warmer, and the piston moves to a higher level. This actual change of state is a spontaneously occurring change of the state of the system composed of the metal block, the mass of air, and the piston.

As in this illustration, an actual change of the state of an isolated system may involve changes of the states of more than one body. When this is the case, the change of state of each body, or of any group of the bodies, can be *separately* considered. When this is done, it shall be said that the change of the state of each body or group of bodies is *supplemented* by the change of the state of the other bodies of the system. Thus, in the above example, the change of state of the mass of air is supplemented by the change of state of the metal block and the cylinder and piston. Or, again, the change of state of the air and the piston is supplemented by the change of state of the cylinder and the metal block. With reference to any given change of the state of any body or group of bodies, the "supplementary change of state" is the associated change of state of the system composed of all the other bodies in any way participating in the process.

### Work-developments

When a change of the state of a body can be described as consisting of the positive or negative action of a force through a distance, the body develops a positive or negative quantity of work, and its change of state shall here be termed a positive or negative "work-development." When the action of a sinking weight or piston is to raise another weight,

or to bring a liquid body to a higher temperature by stirring it, or to decrease the volume and increase the temperature of a mass of gas in a cylinder, the change of state of the sinking body is a positive work-development. When the change of state of the lifted weight, of the stirred liquid, and of the compressed gas is supplemented, in each case, by the change of state of the sinking body, these changes of state are negative work-developments. Work-developments, and changes of state that are not associated with supplementary changes, are termed "adiabatic" changes of state.

### Classification of thermodynamic changes of state

From this point, the qualification "thermodynamic" shall be understood as applying only to the processes explicitly under consideration, namely those involving compression, expansion, change of temperature, fusion, evaporation, the formation of homogeneous mixtures, and changes of chemical state. Any change of state of this type can be supplemented by a work-development, or else by a change of the temperature of another body, or by both together. This consideration suggests that such changes of state may be conveniently arranged in three classes, according as they are supplemented wholly, or in part, or not at all, by actual positive or negative development of work. Let us consider this classification more closely.

*Class 1. Includes every change of state that is supplemented by a work-development.*—When a change of the volume and temperature of a mass of fluid contained in a vertical cylinder is supplemented by a fall or a rise of a heavy piston moving without friction, the change of state of the fluid is supplemented by a positive or a negative work-development, for the action of the piston is the action of its weight through the distance traversed by it. When any compression or expansion of a body is supplemented by an adiabatic change of the volume of another body, the change of state of each body is supplemented by a positive or a negative work-development, for the action of either body may be supposed

replaced by the action of a constant force or else of a continuously varying force.

*Class 2. Includes every change of state that is not supplemented by a work-development, but that is or can be supplemented by a change consisting of a fall of the temperature, or a rise of the temperature, of an extraneous body.*—To ensure that the supplementary operation shall consist solely of a change of temperature, let it be supposed that the supplementary body is enclosed in a thermally conducting rigid shell. Changes of state that can be supplemented by a *fall* of temperature are: a rise of the temperature, with a consequent change of the density, of a body enclosed in a rigid shell; the melting of all or a portion of a solid body similarly enclosed; and any formation of a fluid mixture in a rigid shell, or any chemical process occurring in such a shell, when the final temperature of the mass is above the temperature that would be attained if the process were not associated with a supplementary change. Such changes that can be supplemented by a *rise* of temperature are: a fall of the temperature, with a consequent change of the density, of a body enclosed in a rigid shell; the solidification of all or a portion of a liquid body similarly enclosed; and any formation of a fluid mixture in a rigid shell, or any chemical process occurring in such a shell, when the final temperature of the mass is below the temperature that would be attained if the process were not associated with a supplementary change.

*Class 3. Includes every change of state that is not supplemented by a work-development, but that is or can be supplemented in part by a work-development supplying the positive or negative work actually absorbed, and in part by a change consisting solely of a fall of the temperature, or a rise of the temperature, of a body.*—Such changes are: a non-adiabatic change of the volume and temperature of a fluid; non-adiabatic changes, whether isothermal or not, of the state of aggregation of a body; and any of the changes of state mentioned in the immediately preceding paragraph, when the condition of constant volume of the body is not imposed.

That the proposed classification of changes of state of the type under discussion depends somewhat on the manner in which the changes of state are supplemented is apparent when it is observed, for example, that a change of the temperature of a mass of liquid is a change of the first class when it is supplemented by a development of work expended in stirring the liquid, while it is a change of the second class when it is supplemented by a fall of the temperature of another body, and it is a change of the third class when it is supplemented by a work-development and a fall of temperature acting together.

### The work-value of a thermodynamic change of state

Since a change of state supplemented by a *fall* of the temperature of a body can always be supplemented by a mechanical process in which a development of work is expended in overcoming friction; and since a *rise* of the temperature of a body can always be supplemented by such a mechanical process; it is clear that thermodynamic changes of state can always be brought into connection with purely mechanical operations.

Mutually supplementary *mechanical* changes of state of bodies can be expressed in a way such that a quantitative relationship between the changes of state is established. For example, if a body whose weight is  $w$  falls from a level  $h_1$  to a level  $h_o$ , and this change of state supplements the rise of a body whose weight is  $W$  from the level  $H_o$  to the level  $H_1$ , the work *developed* by the first body is  $(h_1 - h_o)w$ , wherefore the work *absorbed* by the body is

$$-(h_1 - h_o)w.$$

And the work *absorbed* by the second body is

$$+ (H_1 - H_o)W.$$

Defining the "work-value" of the change of state of either body as the quantity of work *absorbed* by the body during the change, and adding these work-values to obtain the work-

value of the change of state of the system of bodies, which work-value is zero, we have

$$-(h_1 - h_0)w + (H_1 - H_0)W = 0,$$

a quantitative relationship between the mutually supplementary changes of state. The possibility of establishing this formulation depends on recognition of the principle that work is neither gained nor lost in any purely mechanical process.

Now, since all thermodynamic changes of state can be brought into connection with purely mechanical operations, may it not be possible, through reference to these operations, to assign to any thermodynamic change of the state of a body a determinate "work-value," in such wise that formulation of the work-value of the change of state of the system composed of all the bodies participating in the process will establish a quantitative relationship between the thermodynamic change and the change of state that supplements it?

In the endeavor to do this let it be determined that when a positive development of work, whether wholly or partly or not at all expended in overcoming friction, can *supplement* a change of the state of a body, the work-value of the change of state shall be the work developed; and that when the development of work can *replace* the change of state of the body—can supplement the supplementary change of state—the work-value of the change shall be the negative of the work developed. In accordance with this determination, to any thermodynamic change of the state of a body shall be assigned a "work-value" defined as follows:

(1) When a change of the state of a body is supplemented by a positive or negative work-development, the work-value of the change of state is the work developed.

(2) When a change of the state of a body is not supplemented by a work-development, but is or can be supplemented by a fall or a rise of the temperature of another body, the work-value of the change of state is



the positive development of work that will replace the fall of temperature, or it is the negative of the positive development of work that will supplement the rise of temperature.

(3) When a change of the state of a body is not supplemented by a work-development, but is or can be supplemented in part by a work-development supplying the positive or negative work actually absorbed, and in part by a fall or a rise of the temperature of another body, the work-value of the change of state is the work that is supplied, plus the positive development of work that will replace the fall of temperature, or minus the positive development of work that will supplement the rise of temperature.

### Illustrations of the definition

It will be well to elucidate the above definition, by application to a few illustrative cases.

A mass of liquid ether overlaid by a mass of ether vapor is confined in a vertical cylinder by a weighted piston moving without friction. When the weight on the piston is increased, the center of gravity of the weighted piston sinks through a difference of level  $h_1 - h_0$ , and the state of the enclosed ether changes to a state of decreased volume, higher temperature, and increased relative mass of the liquid. If the weight of the weighted piston is  $w$ , the work-value of the change of state of the piston is

$$-(h_1 - h_0)w;$$

whereupon the work-value of the change of state of the ether is

$$+ (h_1 - h_0)w.$$

If the weight on the piston had been *decreased*, the change of the state of the ether would have been a change to a state of increased volume, lower temperature, and decreased relative mass of the liquid; and the work-value of the change would have been negative.

Two masses of air in a horizontal cylinder are separated

and maintained at different pressures by a fixed piston. This piston, working without friction, is released, whereupon the masses of air attain equal pressures, and attain temperatures different from their respective initial temperatures. The change of state of the mass of air whose volume is decreased can be supplemented by a mechanical change developing the work  $U$ , having the work-value  $-U$ . So the work-value of the change of state of the compressed air is  $+U$ . The change of state of the mass of air whose volume is increased can be supplemented by a mechanical change absorbing the work  $U$ , having the work-value  $+U$ . So the work-value of the change of state of this mass of air is  $-U$ .

A mass of ice at its melting temperature  $\tau_0$  partially fills a rigid shell in thermal contact with another shell containing a block of metal whose temperature is  $\tau_1 > \tau_0$ . Supplementary changes of state occur, the temperature of the block falling from  $\tau_1$  to  $\tau_0$ ,<sup>1</sup> and a portion of the ice becoming liquid water. Since the change of temperature of the block can be replaced by a mechanical change developing a quantity of work  $U$ , the work-value of this change of temperature is  $-U$  and the work-value of the change of state of the enclosed water is  $+U$ .

Again, the change of state of the water is supplemented by an explosion of a mass of gunpowder contained in the adjoining shell. Since the supplementary change of state of the gunpowder can be replaced by the fall of temperature of the metal block previously considered, the work-value of the change of state is again the work,  $+U$ , whose development will replace the fall of temperature. And the work-value of the change of state of the gunpowder is  $-U$ .

When sulphuric acid and water are mixed, in the absence of a supplementary change the mixture attains a temperature above that of the separate bodies before mixing. When potassium sulphocyanate is similarly dissolved in water, the

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<sup>1</sup> Or, more generally, from  $\tau_1$  to  $\tau^1$ ,  $\geq \tau_0$ , when the operation ceases or is stopped.

resulting solution attains a temperature below that of the separate bodies before mixing. Let these two mixtures be simultaneously formed in two thermally connected rigid shells, the masses of the four component bodies being so chosen that the final temperature of the whole system is the same as the initial temperature—an unessential requirement introduced to simplify the illustration. The change of state of the body composed of the sulphocyanate and water can be supplemented by a fall of the temperature of a block of metal, whose final temperature shall be not below that of the sulphocyanate and water. If the positive development of work that will replace this fall of temperature is  $U$ , the work-value of the change of state of the sulphocyanate and water is  $U$ . The change of state of the body composed of the acid and water can be supplemented by a rise of the temperature of a block of metal, whose final temperature shall be not above that of the acid and water. If the positive development of work that will supplement this rise of temperature is  $U$ , the work-value of the change of state of the acid and water is  $-U$ .

In a vertical cylinder, under a piston moving without friction and supporting the pressure of the atmosphere, a mass of air having the temperature  $\tau_1$  overlies a block of metal whose temperature is  $\tau_2 > \tau_1$ . The mass of air undergoes a thermodynamic change of state supplemented by changes of state of the atmosphere, of the piston, and of the metal block. To simplify the matter, let it be supposed that the changes of state of the cylinder and piston consist only of a displacement of the piston.

If the change of volume of the air is  $\Delta V$ , and that of the metal block is  $\delta V$ , the lower surface of the piston passes through the volume  $\Delta V + \delta V$ . The change of state of the atmosphere being measured by the work done against the atmospheric pressure  $p_1$  through the volume  $\Delta V + \delta V$ , the work-value of this change of state is

$$U_1 = p_1(\Delta V + \delta V).$$

The change of state of the piston consists of a transfer to a higher level. If  $p_2$  is the weight of the piston per unit area of its lower surface, the work-value of this change of state is

$$U_2 = p_2(\Delta V + \delta V).$$

The change of state of the metal block consists of a fall of the temperature of the block, and a change  $\delta V$  of its volume under the pressure  $p_1 + p_2$ . This change of state of the block can be supplemented by a mechanical change developing the work  $-(p_1 + p_2)\delta V$ , together with a rise of temperature supplementable by a development of work  $Q$ . So the work-value of the change of state of the block is

$$U_3 = -(p_1 + p_2)\delta V - Q.$$

The mass of air, now, has increased in volume by  $\Delta V$ , and has attained a temperature above its initial temperature  $\tau_1$ . This change of state can be supplemented by a development of work  $-(p_1 + p_2)\Delta V$ , together with a fall of temperature replaceable by a development of the work  $Q$ . So the work-value of the change of state of the mass of air is

$$U_4 = -(p_1 + p_2)\Delta V + Q.$$

The work-value of the change of state of the system composed of all the bodies participating in the thermodynamic process, determined as the algebraic sum of the work-values of the changes of state of these several bodies, is

$$U_1 + U_2 + U_3 + U_4 = +p_1(\Delta V + \delta V) + p_2(\Delta V + \delta V) \\ - (p_1 + p_2)\delta V - Q - (p_1 + p_2)\Delta V + Q = 0.$$

This is correct, for the change of state of the system is associated with no supplementary change of state.

### **The energy of a body**

When it is shown that a change of the state of a body  $\alpha$  is or can be immediately supplemented by a mechanical change of the state of a body  $\beta_1$ , which develops a positive or negative quantity of work, together with a fall or rise of the temperature of a body  $\beta_2$  enclosed in a rigid shell, or by either

of these changes of state alone; and the "work-value" of the change of state of  $\alpha$  is defined, as above, to be the work developed by  $\beta_1$ , plus the positive development of work that will replace the fall of temperature of  $\beta_2$ , or minus the positive development of work that will supplement the rise of temperature of  $\beta_2$ ; the question arises whether the work-value of the change of state of  $\alpha$ , so defined, is a *determinate quantity*, whether it has a constant value independent of the change of state actually supplementing the change of state of  $\alpha$ , and independent of the path of the change of state of  $\alpha$ . When, for example, an isometric<sup>1</sup> explosion of a given mass of gunpowder successively supplements a rise of the temperature of a body  $\beta_2$  from  $\tau_0$  to  $\tau_1$ , and a rise of the temperature of a body  $\beta_2'$  from  $\tau_0$  to  $\tau_2$ , will the same mechanical process supplement each of these changes of temperature?

When a change of the state of a body can be described as consisting of an immediate absorption or development of work, experiment indicates that the requisite quantity of work is independent of the supplementary operation and of the path of the change of state. Experiment thus indicates that the work-value of the change, as defined, is independent of these circumstances.

Now consider the case in which a change of state  $A_1$  that can be immediately supplemented by a rise of temperature supplements a change of state  $B_1$ . The change  $B_1$  can be supplemented by a mechanical change positively developing work. We may now say that any change of state  $A$ , or in particular any mechanical change  $a$  developing work, that will supplement  $B_1$ , and any change of state  $B$  that will supplement  $A_1$ , will supplement each other, irrespective of the path of any of the changes. This statement is very strongly supported by the results of extended experiments made with the calorimeter, an instrument in which changes of state are supplemented by a change of the temperature of a body, and by the results of experiments in

<sup>1</sup> At constant volume.

which changes of state, especially changes of the temperature of a body, are supplemented by the falling of a weight or by other mechanical operations. Such experiments also indicate that the quantities of work developed in the changes  $a$  are the same. Denote this quantity of work by  $W$ . Now, by the above definition, the work-value of each of the changes of state  $a$ , and the work-value of each of the changes of state  $A$ , each of which can be supplemented by a rise of temperature, is  $U_a = -W$ . And, by the definition, the work-value of each of the changes of state  $B$ , each of which can be immediately supplemented by a fall of temperature, is  $U_b = +W$ . It is thus shown to be supported by extensive experimental evidence that the work-value of *any* of these changes of state is independent of the supplementary operation and of the path of the change of state. And it is shown that, whenever  $U_a$ ,  $U_b$  are the work-values of mutually supplementary changes of state, the algebraic sum of these work-values is the work-value, zero,

$$U_a + U_b = 0,$$

of the process consisting of the mutually supplementary changes.

Finally, consider the case in which a change of state  $A_1$  that can be immediately supplemented by a positive or negative work-development *together* with a rise of temperature supplements a change of state  $B_1$ . The change  $B_1$  can be supplemented by a mechanical change positively or negatively producing work, *together* with a fall of temperature, which fall can in turn be replaced by a mechanical change developing work. We may now say that any change of state  $A$ , or in particular any mechanical change  $a$  positively or negatively developing work, that will supplement  $B_1$ , and any change of state  $B$  that will supplement  $A_1$ , will supplement each other, irrespective of the path of any of the changes. This statement is supported by the results of very extended calorimetric determinations and measurements of work. Such experiments also indicate that the net quantities of

work developed in the changes  $a$  are the same. Denote this quantity of work by  $W$ . Now, by the definition of the work-value of a change of state, the work-value of each of the changes of state  $a$ , and the work-value of each of the changes of state  $A$ , each of which can be replaced by any of the operations  $a$ , is  $U_a = -W$ . And, by the definition, the work-value of each of the changes of state  $B$ , each of which can directly or indirectly be supplemented by any of the operations  $a$ , is  $U_b = +W$ .

It is thus shown to be supported by very extensive experimental evidence that the work-value of any thermodynamic change of the state of a body is independent of the supplementary operation and of the path of the change of state. And it is shown that, whenever  $U_a$ ,  $U_b$  are the work-values of mutually supplementary changes of state, the algebraic sum of these work-values is the work-value, zero,

$$U_a + U_b = 0,$$

of the process consisting of the mutually supplementary changes.

When it is established that the work-value of any thermodynamic change of state is a determinate quantity, it is established that

*The work-value of any thermodynamic change of the state of any body is equal to the corresponding change*

$$E_2 - E_1$$

*of the value of a quantity  $E$ , which quantity is determined by the state of the body, has one value for each state, and contains an arbitrary additive constant.*

The quantity  $E$  is termed the "energy" of the body.

### The first law of thermodynamics

Let  $U$  be the work-value of any thermodynamic change of state. We distinguish three cases, in which the change of state is supplemented wholly or in no part or in part by actual positive or negative development of work.

*Case 1.*—The change of state is supplemented by a positive or negative development of work  $U_1$ , and so can be described as a positive or negative absorption of the work  $U_1$ .

*Case 2.*—The change of state is or can be supplemented by a fall of temperature, replaceable by a positive development of work  $U_2$ , or it is or can be supplemented by a rise of temperature, supplementable by a positive development of work  $U_2$ .

*Case 3.*—The change of state is or can be supplemented by a change that is a positive or negative development of work  $U_1$ , together with another change consisting of a fall of temperature, replaceable by a positive development of work  $U_2$ , or consisting of a rise of temperature, supplementable by a positive development of work  $U_2$ .

In the first case, the work-value of the change of state in question is the work immediately absorbed,

$$U = + U_1;$$

in the second case, the work-value of the change is the work absorbed or absorbable through intervention of a change of the temperature of a body,

$$U = \pm U_2;$$

in the third case, the work-value is the work immediately absorbed, plus the work absorbed or absorbable through intervention of a change of the temperature of a body,

$$U = + U_1 \pm U_2.$$

In general, then, the work-value of a thermodynamic change of state is the sum of two terms: the positive or negative work immediately absorbed, and the positive or negative work absorbed or absorbable through intervention of a change of the temperature of a body. These terms are given separate names. The positive or negative work immediately absorbed by a body is termed the "work" added to the body, and the positive or negative work absorbed or absorbable by the



body through intervention of a change of the temperature of another body is termed the "heat" added to the body.

Accordingly, the work-value of a thermodynamic change of the state of a body is the algebraic sum of the work and heat added to the body during the change; wherefore the sum of the work  $W$  and heat  $Q$  added to a body in a thermodynamic change of its state is equal to the corresponding change of the energy of the body,

$$E_2 - E_1 = W + Q.$$

Here  $W$ ,  $Q$  are quantities of work whose numerical values are regarded as obtained by experiment.

When the implications of this equation are compared with experience, they are found everywhere to be confirmed in great detail and to the highest attainable exactness. It is thus recognized that the equation formulates a very general natural "law,"—a very general quantitative description of the manner in which thermodynamic processes take place, a very general type of relation between measurable physical quantities.

The statement that the sum of the work and heat added to a body in any thermodynamic change of its state is uniquely determined by the end states of the body is known as the "first law of thermodynamics." The statement that the algebraic sum of the work-values of mutually supplementary changes of state is zero, or in other words that the algebraic sum of the changes of the energies of bodies undergoing mutually supplementary changes of state is zero, is the "law of the conservation of energy," as applied to thermodynamic changes.

### Illustrations

Since it is important to understand clearly the meanings of the terms "work," "heat," and "energy," let us consider the employment of these terms in connection with various particular thermodynamic changes of state.

A mass of liquid ether overlaid by a mass of ether vapor is confined in a vertical cylinder by a weighted piston moving without friction. When the weight on the piston is increased,

the center of gravity of the weighted piston sinks through a difference of level  $h_1 - h_0$ , and the state of the enclosed ether changes to a state of decreased volume, higher temperature, and increased relative mass of the liquid. If the weight of the weighted piston is  $w$ , the change of the energy of the piston is equal to the work added to it,

$$-(h_1 - h_0)w;$$

and the change of the energy of the ether is equal to the work added to the ether,

$$+ (h_1 - h_0)w.$$

Two masses of air in a horizontal cylinder are separated and maintained at different pressures by a fixed piston. This piston, moving without friction, is released, whereupon the masses of air attain equal pressures, and attain temperatures different from their respective initial temperatures. The change of the energy of the mass of air that is compressed is equal to the work  $W$  added to it; and the change of the energy of the expanded mass is equal to the work  $-W$  added to it.

A mass of ice at its melting temperature  $\tau_0$  partially fills a rigid shell in contact with another shell containing a block of metal whose temperature is  $\tau_1 > \tau_0$ . Supplementary changes of state occur, the temperature of the block falling from  $\tau_1$  to  $\tau_1' \geq \tau_0$ , when the operation ceases or is stopped. A portion of the ice becomes liquid water. Since the change of temperature of the block can be replaced by a mechanical change developing a quantity of work  $Q$ , the change of the energy of the block is equal to the heat  $-Q$  added to the block; and the change of the energy of the enclosed water is equal to the heat  $+Q$  added to the water.

Again, the change of state of the water is supplemented by an explosion of a mass of gunpowder contained in the adjoining shell. Since the supplementary change of state of the gunpowder can be replaced by the fall of the temperature of the metal block previously considered, the change of the energy of the gunpowder is equal to the heat  $-Q$  added

to the powder; and the change of the energy of the water is equal to the heat  $+Q$  added to the water.

When mixtures, of sulphuric acid and water and of potassium sulphocyanate and water, are formed in two thermally connected rigid shells, the mixtures will attain a common temperature. The change of state of the body composed of the sulphocyanate and water can be supplemented by a fall of the temperature of a block of metal. If a development of the work  $Q$  is requisite to replace this fall of temperature, the change of the energy of the sulphocyanate and water is equal to the heat  $Q$  added to this body in the original process; and the change of the energy of the body composed of the acid and water is equal to the heat  $-Q$  added to this body.

In a vertical cylinder, under a piston moving without friction and supporting the pressure  $p_1$  of the atmosphere, a mass of air having the temperature  $\tau_1$  overlies a block of metal whose temperature is  $\tau_2 > \tau_1$ . The atmosphere, the piston, the metal block, and the enclosed air undergo changes of state.<sup>1</sup> If the change of the volume of the air is  $\Delta V$ , and that of the metal block is  $\delta V$ , the lower surface of the piston passes through the volume  $\Delta V + \delta V$ . The change of the energy of the atmosphere is equal to the work

$$p_1(\Delta V + \delta V)$$

added to the atmosphere. If  $p_2$  is the weight of the piston per unit area of its lower surface, the change of the energy of the piston is equal to the work

$$p_2(\Delta V + \delta V)$$

added to the piston. The change  $\delta V$  of the volume of the block, and the fall of its temperature, can be replaced by a mechanical change developing the work  $(p_1 + p_2)\delta V$ , together with a mechanical change developing a quantity of work  $Q$ . So the change of the energy of the block is equal to the work

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<sup>1</sup> As in the previous employment of this illustration, it shall be supposed that the changes of state of the cylinder and piston consist only of a displacement of the piston.

$-(p_1 + p_2)\delta V$  added to it in the original change of state of the system, plus the heat  $-Q$  added to it in this change,

$$-(p_1 + p_2)\delta V - Q.$$

The mass of air has increased in volume by  $\Delta V$ , and has attained an increased temperature. This change of state can be supplemented by a mechanical operation developing the work  $-(p_1 + p_2)\Delta V$ , together with a change consisting of a fall of the temperature of a body and replaceable by a development of work  $Q$ . So the change of the energy of the mass of air is equal to the work  $-(p_1 + p_2)\Delta V$  added to the mass, plus the heat  $Q$  added to it,

$$-(p_1 + p_2)\Delta V + Q.$$

The change of the energy of the group of four bodies is equal to the sum of the energy changes of the bodies. It is also equal to the sum of the work and heat added to the group in its change of state. Neither work nor heat has been added, so the sum of the energy changes is zero,

$$0 = p_1(\Delta V + \delta V) + p_2(\Delta V + \delta V) - (p_1 + p_2)\delta V - Q - (p_1 + p_2)\Delta V + Q.$$

This equation is satisfied identically.

### Heat

It is especially to be noted that positively "adding heat" to a body—"heating" the body—is not in general associated with a rise of the temperature of the body. Nor does a change of the temperature necessarily involve absorption or development of heat. When a mass of air is adiabatically compressed, or when it expands into a vacuum, the temperature of the mass changes, but no heat is added to it. When heat is added to a block of metal, the temperature of the block rises. When heat is added to a mass of liquid water and overlying water vapor supporting a constant pressure, the temperature of the mass is not altered. Heat may be added to a mass of potassium sulphocyanate and water in the process of forming a mixture, and the temperature fall. An addition of heat to a body involves a change of the state of the body,

but it may not involve a change of the temperature alone, and it may not involve a change of the temperature at all.

By the positive or negative "quantity of heat" added to a body in a change of its thermodynamic state is *meant* the development of work that will replace the fall, or supplement the rise, of the temperature of another body, which fall or rise, together with a positive or negative or zero work-development, immediately supplements or can supplement the change of state of the body. Stated in a less detailed way, the quantity of "heat" added to a body in a change of its thermodynamic state is the work absorbed or absorbable by the body through direct intervention of a change of the temperature of another body.

This is all that a "quantity of heat" means. To assume it to mean a quantity of an imponderable fluid, or a quantity of the kinetic energy of hypothetical and inaccessible particles, is to replace direct statement of physical facts, made with the aid of clearly defined terms, by a hypothetical interpretation of the facts. And it should not be forgotten that quantities of "work," of "heat," and of "energy," are *auxiliary* quantities, introduced by definition, and employed solely because they are useful in the establishment of *relations between the measurable physical variables* that are concerned in thermodynamic changes of state. It is these *relations* that are sought in the study of thermodynamic changes, and all else is accessory and nothing more.

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