

# The Second Law: Statement and Applications

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Pierre Infelta

Département de Chimie, École Polytechnique Fédérale de Lausanne, Institut de Chimie Physique, CH 1015 Lausanne, Switzerland; pierre.infelta@epfl.ch

Attempts to clarify the second law of thermodynamics remain of interest (1). The second law has been presented in a great variety of ways. It is often stated as the fact that the entropy of an *isolated system* increases when a *spontaneous* change takes place. While this statement is true, we show that it is definitely restrictive. Moreover, the meaning of “spontaneous” is sometimes ambiguous and misleading (2).

It is probably wise to distinguish only two kinds of thermodynamic processes: *reversible* and *irreversible* (and thus spontaneous) processes. The latter occur (or at least tend to occur<sup>1</sup>) as a result of some change in the constraints applied to the system under investigation—such as, for example, a change in the external pressure or external forces applied to the system, an interaction with a thermal bath, or an interaction suddenly made possible between two subsystems. The system is out of equilibrium, and as a consequence, an irreversible process takes place spontaneously. Following a number of textbook authors (3–7), we show here that a more appropriate statement of the second law is:

An irreversible and thus spontaneous process in a closed adiabatic system results in an increase of its entropy.

This form of the second law leads to a very straightforward understanding of the significance of the Gibbs free energy. We illustrate it further by a simple example. Additional applications and examples are provided in the supplemental material.<sup>W</sup>

## Basic Considerations

It is of interest to understand how systems interact with their environment, other systems, and thermal reservoirs. In our context, we consider only thermal reservoirs that remain at constant temperature and have an infinite heat capacity. As a starting point, we use the convenient formulation of the second law known as the Kelvin formulation. In a single sentence, it can be stated the following way:

Using a system that undergoes a cyclic thermodynamic process, it is impossible to obtain useful work if, overall, the system only exchanges heat with one thermal reservoir.

From this statement, we are going to derive various elaborate results, which turn out to be more convenient to use than the Kelvin formulation for specific problems.

At this stage, it is useful to provide a few comments about the Kelvin formulation. During the process considered, the system need not always be in contact with the thermal reservoir. The temperature of the system may be different from that of the thermal reservoir during any part of the cyclic process. Even when the system is in contact with the thermal reservoir, its temperature may not be uniform or identical to that of the thermal reservoir owing to the irreversible nature of the process. Since the system undergoes a cyclic process, its initial and final states must, however, be the same, with well-defined thermodynamic variables.

We recall that energy received by a system from its surroundings is counted positively and, conversely, energy provided by a system is counted negatively. The Kelvin formulation of the second law implies that the work done on such a system during this type of process cannot be negative. It is either positive or zero. Mathematically, we can write

$$w \geq 0 \quad \begin{cases} \text{cyclic process} \\ \text{single thermal reservoir affected when cycle is completed} \end{cases} \quad (1)$$

Taking into account the first law of thermodynamics, the change in the internal energy of the system is zero after the cyclic process is completed, since the initial (*I*) and final (*F*) states of the system are identical. Hence, we have

$$U_F - U_I = \Delta U = w + q = 0 \Rightarrow q \leq 0 \quad (2)$$

In general, such a cycle can only be achieved if some positive work *w* is done on the system and a corresponding amount of heat is delivered to the thermal reservoir.

If the process is reversible, the work done on the system is zero, *w* = 0. This last point can be shown the following way. Consider the system undergoing a reversible cyclic process along a *set path* in a given direction, *direction 1*. Let *w*<sub>dir1</sub> be the work done on the system during this cycle. During a reversible process, the external forces always exactly balance the internal forces. Thus, we can effect a reversible cyclic process along *the same path* with the direction of all of the displacements reversed. The work done on the system is in this case *w*<sub>dir2</sub>. Since the signs of all displacements are reversed, while the external forces are not modified, we have

$$w_{\text{dir1}} = -w_{\text{dir2}} \quad (3)$$

We apply the formulation of eq 1 to both of the cycles just described above:

$$\begin{aligned} w_{\text{dir1}} &\geq 0 \\ w_{\text{dir2}} &\geq 0 \end{aligned} \quad (4)$$

Making use of eq 3 in the first inequality of eq 4, we obtain

$$-w_{\text{dir2}} \geq 0 \quad (5)$$

By comparing the last inequality of eq 4 with eq 5, we obtain

$$w_{\text{dir2}} = 0 = w_{\text{dir1}} \quad (6)$$

This result leads us to the conclusion that during a reversible cyclic process of a system that can exchange heat with at most one thermal reservoir, the system globally does not exchange heat and no work is done on it either. The inequalities in eqs 1 and 2 apply therefore to irreversible cycles.

## Entropy Change of a Closed Adiabatic System during a Reversible Process

Let us consider a *closed adiabatic system* (closed system with adiabatic walls). The entropy change of the system, during

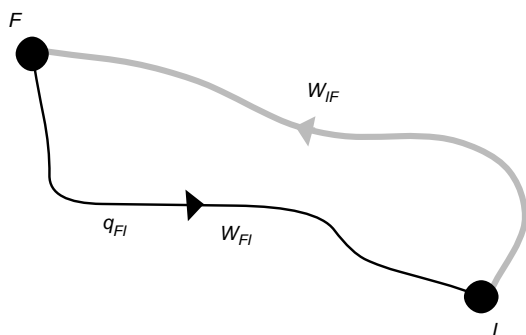


Figure 1. Schematic representation of the cycle envisaged. During the irreversible part, the system is closed adiabatic; its intermediate states are ill defined. It is followed by a reversible part where the system can exchange heat with a thermal reservoir.

a reversible process from state  $I$  to state  $F$ , is zero because the reversible heat transfer is identically zero.

$$S_F - S_I = \int_I^F \frac{dq_{\text{rev}}}{T_{\text{sys}}} = 0 \quad (7)$$

A reversible adiabatic process is also called an *isentropic* process.

### Other Form of the Second Law. Irreversible Change of a Closed Adiabatic System

In many texts, the second law is stated as

The entropy change for an irreversible process occurring in an isolated system is positive.

An *isolated system* is a system that does not exchange matter, heat, or work with its surroundings. Let us show that the above statement of the second law is too restrictive.

For this purpose, we consider a closed adiabatic system. Such a system does not exchange matter or heat with its surroundings. Work can, however, be done on it. Let us assume this system is not at equilibrium. It evolves spontaneously and irreversibly from an initial state  $I$  to a final state  $F$ . During this process, the work done on the system is  $w_{IF}$ . Let us now examine whether it is possible to bring this system back from state  $F$  to state  $I$  through some process, reversible or irreversible, thus completing an irreversible cyclic process (since at least the first part of it is irreversible).

The first law of thermodynamics tells us that the change in the internal energy of the system is zero for any cycle. The adiabatic system receives no heat during this cycle and we have

$$\left. \begin{array}{l} q_{\text{cycle}} = 0 \\ \Delta U_{\text{cycle}} = 0 \end{array} \right\} \Rightarrow w_{\text{cycle}} = 0 \quad (8)$$

According to the result obtained in eq 6 such a cycle should be reversible, in contradiction with our hypothesis that it is irreversible. It is therefore impossible to bring the system back to its initial state. We thus find the interesting result that

It is impossible to conceive or realize an irreversible cyclic process of a closed adiabatic system.

Let us envisage now if it is possible to bring back the system from state  $F$  to state  $I$  by a reversible process during

which the system is no longer adiabatic. Assume that the system may, at some point, exchange an amount of heat  $q_{FI}$  with one thermal reservoir at temperature  $T_{\text{therm}}$ . Note that since this part of the cycle is assumed to be reversible, such a contact is only possible if the system temperature is identical to that of the thermal reservoir when they are brought into contact for the heat exchange to take place. The heat exchange takes place during an isothermal process (otherwise it would not be reversible). The remainder of the reversible part of the cycle can only be adiabatic (isentropic) changes (to bring the system to the temperature of the thermal reservoir and then to the temperature of state  $I$ ). The cycle envisaged here is schematically represented in Figure 1.

Let us write explicitly that, according to the first law, the internal energy change is zero for this cycle. We have

$$\Delta U = w_{IF} + w_{FI} + q_{FI} = 0 \quad (9)$$

According to eq 1, the total work done on the system during this irreversible cycle is positive and we have

$$\begin{array}{l} w_{IF} + w_{FI} > 0 \\ q_{FI} < 0 \end{array} \quad (10)$$

During the adiabatic portions of the reversible part of the cycle, the entropy of the system does not change. It only changes during the isothermal portion of the process, when the system temperature is the same as that of the thermal reservoir. The entropy change of the system during the reversible portion of the cycle is therefore

$$S_I - S_F = \int_F^I \frac{dq_{\text{rev}}}{T_{\text{therm}}} = \frac{q_{FI}}{T_{\text{therm}}} < 0 \quad (11)$$

Since entropy is a state function, the result of eq 11 shows that the entropy change during the irreversible process is such that

$$S_F > S_I \quad (12)$$

We find that when a closed adiabatic system evolves irreversibly, its entropy in its final state is larger than in its initial state. The second law of thermodynamics can therefore be expressed as

An irreversible and thus spontaneous process of a closed adiabatic system results in an increase of its entropy.

This form of the second law, as we are going to see, is very versatile and quite simple to apply. The frequently encountered form of the second law is too restrictive. The present statement encompasses the usual and limited statement for an isolated system since an isolated system is of course closed and adiabatic with the added constraint that the work done on it is zero.

### General Result for a Closed Adiabatic System

Using the result of eq 7, we can modify eq 12 to cover both irreversible and reversible processes of any closed adiabatic system:

$$S_F \geq S_I \quad (13)$$

where the equality applies to the case of a reversible process. We can also state in a somewhat unusual but interesting way the second law of thermodynamics.

It is impossible to conceive or realize a thermodynamic process of a closed adiabatic system that results in a decrease of its entropy.

### Equilibrium Condition for a Closed Adiabatic System

Any irreversible evolution of a closed adiabatic system results in an increase in its entropy. Equilibrium is thus attained when the entropy of the system can no longer increase. The entropy therefore must have reached its maximum possible value. We can state the equilibrium condition as

A closed adiabatic system is at equilibrium when its entropy has reached its maximum possible value.

### Changes in a Closed System in Contact with a Single Thermal Reservoir

Let us now envisage a process where the closed system under investigation is, at least during part of the process, in contact with one thermal reservoir at temperature  $T_{\text{therm}}$ . The system and the thermal reservoir can be considered together as a *closed and adiabatic global system*. Let us write explicitly the entropy change for this global system:

$$\begin{aligned} q_{\text{sys}} &= -q_{\text{therm}} \\ (S_F - S_I)_{\text{global}} &= (S_F - S_I)_{\text{sys}} + (S_F - S_I)_{\text{therm}} \\ &= (S_F - S_I)_{\text{sys}} + \frac{q_{\text{therm}}}{T_{\text{therm}}} \\ &= (S_F - S_I)_{\text{sys}} - \frac{q_{\text{sys}}}{T_{\text{therm}}} \end{aligned} \quad (14)$$

where  $q_{\text{sys}}$  is the amount of heat received by the system during the process. The entropy change of the thermal reservoir is obtained from the amount of heat it receives since its temperature is constant no matter how the process takes place. Since the change in entropy of the global system has to be positive, we get from eq 14

$$\begin{aligned} (S_F - S_I)_{\text{sys}} - \frac{q_{\text{sys}}}{T_{\text{therm}}} &\geq 0 \\ \Downarrow \\ q_{\text{sys}} &\leq T_{\text{therm}}(S_F - S_I)_{\text{sys}} = q_{\text{sys}}(\text{rev}) \end{aligned} \quad (15)$$

The last equality in eq 15 comes from the fact that when the system reversibly goes from the same initial state to the same final state, an entropy change occurs only when the system is in contact with the thermal reservoir and its temperature is then equal to the temperature of the thermal reservoir. The other parts of the reversible process are reversible adiabatic (isentropic) changes.

We find here the interesting result that a system that can be in contact with a single thermal reservoir receives an amount of heat that is always smaller during an irreversible process than during a reversible process between the same states.

### Additional Results for Cyclic Processes

#### Cyclic Process of a System that Comes in Contact with One Thermal Reservoir

Consider a system undergoing a cyclic process during part of which it is in contact with a thermal reservoir. The

amount of heat received by the system during the cycle is  $q_{\text{sys}} \leq 0$  (from eq 2). The amount of heat received by the thermal reservoir during the cycle is  $-q_{\text{sys}}$ . The entropy change of the thermal reservoir is

$$\Delta S_{\text{therm}} = -\frac{q_{\text{sys}}}{T_{\text{therm}}} \geq 0 \quad (16)$$

During the cycle, the change in the entropy of the system is zero. Consider the closed system together with the thermal reservoir it can exchange heat with. This global system is closed and adiabatic. We find that the entropy change of the global system,  $\Delta S_{\text{global}}$ , is positive for an irreversible process and zero for a reversible one:

$$\Delta S_{\text{sys}} + \Delta S_{\text{therm}} = \Delta S_{\text{global}} \geq 0 \quad \text{for a cyclic process of a system in contact with one thermal reservoir} \quad (17)$$

#### Cyclic Process of a System that Comes in Contact with Several Thermal Reservoirs

Let us examine the case of a cyclic process of a system that exchanges heat with several thermal reservoirs,  $i$ . The result of eq 15 can be applied to each heat-exchange step. The entropy change of the system for a cyclic process is zero. We have

$$\frac{q_{\text{sys},i}}{T_{\text{therm},i}} \leq \Delta S_{\text{sys},i} \Rightarrow \sum_i \frac{q_{\text{sys},i}}{T_{\text{therm},i}} \leq 0 = \Delta S_{\text{sys}} \quad (18)$$

The last inequality of eq 17 is the *Clausius inequality*. By noting that the amount of heat received by thermal reservoir  $i$  is  $-q_{\text{sys},i}$ , this result can also be written

$$\sum_i \frac{-q_{\text{sys},i}}{T_{\text{therm},i}} = \sum_i -\Delta S_{\text{therm},i} \leq 0 \Rightarrow \sum_i \Delta S_{\text{therm},i} \geq 0 \quad (19)$$

The result of eq 19 can be reformulated as

$$\Delta S_{\text{global}} \geq 0 \quad \text{cyclic process of a system that comes in contact with several thermal reservoirs} \quad (20)$$

This result is no surprise, since the ensemble of the thermal reservoirs and the system taken together constitute a global adiabatic system. The inequality applies to irreversible cycles, whereas the equality applies to reversible cycles of the system.

### Application of the Above Results

We illustrate now the advantages of the present formulation of the second law and its simplicity of use. We use it to get the significance of the Gibbs energy for a *monothermal monobaric system*. We also show how the equilibrium state for a simple closed adiabatic system corresponds to the maximum possible value of its entropy. Additional illustrations are provided in the supplemental material.<sup>W</sup>

#### Gibbs Energy

Let us consider a process where a closed system can come in contact with only one thermal reservoir at temperature  $T_{\text{therm}}$ . The change in the entropy of the global system (closed and adiabatic) that consists of the system and the thermal reservoir is

$$(S_F - S_I)_{\text{global}} = (S_F - S_I)_{\text{sys}} + (S_F - S_I)_{\text{therm}} \quad (21)$$

The change in the entropy of the thermal reservoir can be expressed in terms of some of the system variables that characterize the process. We have

$$(S_F - S_I)_{\text{therm}} = \frac{q_{\text{therm}}}{T_{\text{therm}}} = -\frac{q_{\text{sys}}}{T_{\text{therm}}} = -\frac{(U_F - U_I)_{\text{sys}} - w}{T_{\text{therm}}} \quad (22)$$

Using eq 22 to express  $(S_F - S_I)_{\text{therm}}$  in eq 21, we obtain the following expression for the work done on the system:

$$w = (U_F - U_I)_{\text{sys}} - T_{\text{therm}}(S_F - S_I)_{\text{sys}} + T_{\text{therm}}(S_F - S_I)_{\text{global}} \quad (23)$$

Let us now assume that the process can be described as *monothermal*, by which we mean that in its initial and final states, the system is assumed to be in thermal equilibrium with the thermal reservoir,  $T_{I,\text{sys}} = T_{F,\text{sys}} = T_{\text{therm}}$ . Note that during the process, the system may not be in contact with the thermal reservoir all the time. The system need not be at the temperature of the thermal reservoir during the process even when it is in contact with it (for example, because the process is irreversible or the system temperature may be ill defined). We have, in view of the monothermal character of the process,

$$\begin{aligned} U_{I,\text{sys}} &= G_{I,\text{sys}} - p_{I,\text{sys}} V_{I,\text{sys}} + T_{\text{therm}} S_{I,\text{sys}} \\ U_{F,\text{sys}} &= G_{F,\text{sys}} - p_{F,\text{sys}} V_{F,\text{sys}} + T_{\text{therm}} S_{F,\text{sys}} \\ \Downarrow \\ w &= (G_F - G_I)_{\text{sys}} - p_{F,\text{sys}} V_{F,\text{sys}} + p_{I,\text{sys}} V_{I,\text{sys}} + T_{\text{therm}}(S_F - S_I)_{\text{global}} \end{aligned} \quad (24)$$

The relation just obtained can be further modified if the external pressure acting on the system is constant during the entire process and equal to the system pressure at the beginning and at the end of the process, so that  $p_{F,\text{sys}} = p_{I,\text{sys}} = p_{\text{ext}}$ . Such a process can be called a *monobaric process*. It differs from an isobaric process inasmuch as the pressure in the system need not always be equal to the external pressure. The  $pV$  terms can then be identified with the work due to volume change done on the system. We have, in view of the monobaric character of the process,

$$w = (G_F - G_I)_{\text{sys}} - p_{\text{ext}}(V_F - V_I)_{\text{sys}} + T_{\text{therm}}(S_F - S_I)_{\text{global}} = (G_F - G_I)_{\text{sys}} + w_{\text{vol}} + T_{\text{therm}}(S_F - S_I)_{\text{global}} \quad (25)$$

We refer to all forms of work other than work due to the change in volume of the system as  $w_{\text{other}}$ . We can write

$$w_{\text{other}} = w - w_{\text{vol}} = (G_F - G_I)_{\text{sys}} + T_{\text{therm}}(S_F - S_I)_{\text{global}} \quad (26)$$

We stated earlier that the equilibrium condition is that the entropy of the global system be maximum. The equilibrium condition for a monothermal and monobaric process of a system can also be written

$$-T_{\text{therm}}(S_F - S_I)_{\text{global}} = (G_F - G_I)_{\text{sys}} - w_{\text{other}} \Rightarrow \text{minimum} \quad (27)$$

since the change in global entropy is either positive for an irreversible process or zero for a reversible one. We also have

$$w_{\text{other}} \geq (G_F - G_I)_{\text{sys}} \quad (28)$$

For a monothermal and monobaric process of a system in contact with a thermal reservoir, we can summarize different possible cases:

$w_{\text{other}}$	$(G_F - G_I)_{\text{sys}}$
$> 0$	Minimum amount of work needed to achieve the change
$< 0$	Maximum amount of work one can hope to obtain
$= 0$	Reversible process: Gibbs energy does not change.
	Irreversible process: Gibbs energy decreases until it reaches a minimum.

In chemical applications, systems are frequently monothermal and monobaric with no other work done on them than volume work. We can state:

A monothermal and monobaric system, on which no work other than work due to volume change is done, evolves spontaneously as long as its Gibbs energy can decrease.

Note that this statement is less restrictive than the usual statement for “isothermal and isobaric” systems and is more likely to correspond to practical cases. It is actually difficult to imagine that an irreversible process could be strictly isothermal and isobaric.

### Process in a Closed Adiabatic System

Consider a cylinder containing  $n$  moles of an ideal gas and closed by a piston. Both piston and cylinder have adiabatic walls with negligible heat capacities. Frictions with the walls are also neglected. The heat capacity of the gas is assumed to be constant. The initial state of the system is represented schematically in Figure 2, the piston being blocked. The piston is released. The external pressure is assumed to remain constant during the process. We want to find the state of equilibrium of this system. We propose to verify that at equilibrium, the internal pressure is equal to the external pressure and the entropy of the gas is maximum, in agreement with our form of the second law. The entropy change for an ideal gas between two states characterized by pressure and temperature is

$$S - S_I = n \left( C_{p,m} \ln \frac{T}{T_I} - R \ln \frac{p}{p_I} \right) \quad (29)$$

For each would-be equilibrium position of the piston, the temperature of the gas is linked to its volume by the first law and the ideal gas law. We have

$$\begin{aligned} q &= 0 \\ U - U_I &= w \\ \Downarrow \\ nC_{V,m}(T - T_I) &= -p_{\text{ext}}(V - V_I) = -nR p_{\text{ext}} \left( \frac{T}{p} - \frac{T_I}{p_I} \right) \end{aligned} \quad (30)$$

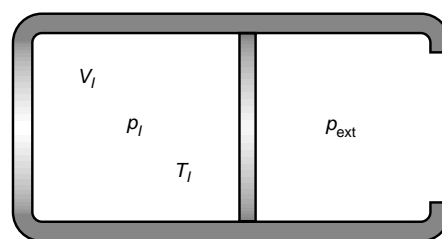


Figure 2. The system is the ideal gas contained in the cylinder. All walls are adiabatic.

We thus find the relation that exists between the gas temperature  $T$  and its pressure  $p$ . We have

$$T = T_I \frac{C_{V,m} + R \frac{p_{\text{ext}}}{p_I}}{C_{V,m} + R \frac{p_{\text{ext}}}{p}} \quad (31)$$

We can now express the entropy change using the gas pressure  $p$  as the variable. We have

$$S - S_I = n \left( C_{p,m} \ln \frac{C_{V,m} + R \frac{p_{\text{ext}}}{p_I}}{C_{V,m} + R \frac{p_{\text{ext}}}{p}} - R \ln \frac{p}{p_I} \right) \quad (32)$$

Let us find the value of  $p$  that corresponds to an extremum of the entropy change. For that we must have

$$\frac{\partial(S - S_I)}{\partial p} = -\frac{nR}{p} \frac{C_{V,m}p - (C_{p,m} - R)p_{\text{ext}}}{C_{V,m}p + Rp_{\text{ext}}} = 0 \quad (33)$$

The entropy change has an extremum when

$$p = p_{\text{ext}}, \text{ remembering that for an ideal gas} \quad (34)$$

$$C_{p,m} - R = C_{V,m}$$

The sign of the derivative in eq 34 in the vicinity of the equilibrium pressure shows that this extremum is a maximum.

We selected numerical values to illustrate our findings in Figure 3 for two values of the external pressure. We see that the calculated entropy reaches a maximum when the internal pressure,  $p$ , is equal to the external pressure. The system is then at equilibrium.

The spontaneous process is an expansion if the external pressure is smaller than the internal pressure and a compression if the external pressure is larger than the initial gas pressure. The entropy of this closed adiabatic system increases during these irreversible processes, as expected from the second law.

## Conclusion

We have illustrated that a frequently encountered statement of the second law is too restrictive. The second law as we state it for a closed adiabatic system proves to be versatile and easy to use to judge the feasibility of thermodynamic processes. The entropy of a closed adiabatic system spontaneously tends to increase if the system is out of equilibrium, resulting in an irreversible process. The system is at equilibrium when its entropy can no longer increase and has reached its maximum value. We used this criterion on a simple example.

For systems in contact with one thermal reservoir, the entropy of the global system, which includes the system of interest plus the thermal reservoir, increases during any spontaneous irreversible process. We obtained the significance

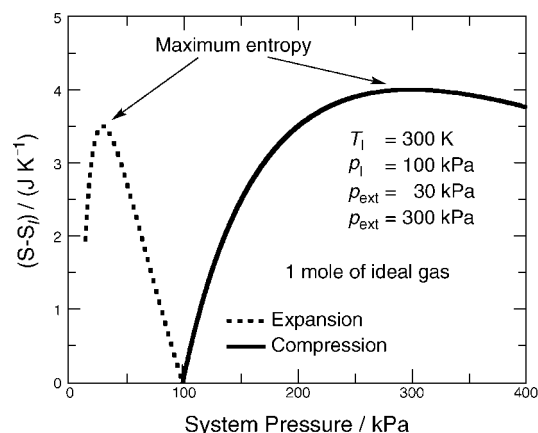


Figure 3. Closed adiabatic system. Entropy change vs system pressure. At equilibrium  $p = p_{\text{ext}}$ . Entropy is then at a maximum. For the conditions selected, the equilibrium temperatures are 240 K for the expansion and 471 K for the compression.

of the Gibbs function and a clear justification for its use in predicting the evolution of monothermal and monobaric systems.

We also find that for an irreversible cyclic process of a system that comes in contact with several thermal reservoirs, the global entropy change is always positive.

The derivations presented here deal mostly with initial and final states, reducing the use of differential expressions, and are usually understood more easily by students.

## Supplemental Material

Additional examples of the application of this formulation of the second law are available in this issue of *JCE Online*.

## Note

1. We make provision here for systems that are in metastable states or systems for which the process takes place on a time scale much longer than human observation time.

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