

First Law of Thermodynamics; Irreversible and Reversible Processes

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By its very nature thermodynamics engenders careful logical thinking. Yet in presentations in textbooks, even at the highest levels, troublesome gaps appear in the logic of the development. Such gaps are not only weaknesses in the logical structure of the subject, but they are impediments to thoughtful students learning thermodynamics.

The laws of thermodynamics are, as the term “law” implies, generalizations based on experimental evidence. Thus it is essential that the laws and related concepts be well grounded in experimental observations. Definitions should be “operational”, that is, traceable to experimental observations. In this paper, we recall how the first law of thermodynamics arises from experimental observations. We evaluate an alternative, adiabatic-work formulation of the first law. We compare algebraically and graphically irreversible and reversible paths for isothermal and adiabatic processes in an ideal gas. We examine the concept of a reversible process and show how a reversible process is based solely on the first law.

The paper uses the language of the “local” formulation of thermodynamics as distinct from the “global” formulation (1, 2). The local formulation is the standard formulation in which *the* system is typically the chemical system, the center of attention. In our journeys to a deeper understanding of the local formulation of thermodynamics, as explicated here, we have found experience with the “global” point of view to be a helpful guide. These understandings are reflected in this paper. We will borrow a few concepts directly from the global formulation, in which various subsystems are given distinctive names. To begin, we will call *the* system in which the chemical reaction takes place the reactive system.

In structuring this paper, we assume the reader has sufficient knowledge of the concept of a reversible process to permit its use before we turn to a full consideration of its proper basis within the context of the first law.

The First Law

Many experiments have shown that the heat effect q and the work effect w vary for different paths between a given initial state and a given final state of a reactive system, yet the sum of q and w is always independent of the path between the same initial and final states. In thermodynamics, we presume these remarkable observations are always true and generalize them into a law. Consequently, we write

$$dU = Dq + Dw \quad (1a)$$

or, in integral form,

$$\Delta U = q + w \quad (1b)$$

The “d” symbol for a differential reminds us that the change in the internal energy U , which is a state function defined through the first law, is independent of the path. In contrast, the “D” symbol reminds us that the heat effect and the work effect are inexact differentials which depend on the path.

In this presentation of the experimental basis of the first law, we have used the terms “heat effect” and “work effect”. We have done so to emphasize that these quantities relate to *processes* and not to energy contents. In thermodynamics, “heat” and “work” are processes by which energy is transferred between a reactive system and its interacting surroundings. Once a process of energy transfer is over, the terms heat and work no longer apply. Such terms as “heat content” or “heat bath” are throwbacks to caloric theory in which heat was regarded as a conserved fluid. “Heat of reaction” is little better. Useful alternatives to the terms “heat effect” and “work effect” are the active words “heating” and “working”. If “heating” or “working” can sensibly replace “heat” or “work” in thermodynamic usage, the concepts are being correctly applied. Such terminology as “heating content”, “heating bath”, and “heating of reaction” sound odd and signal inappropriate usages. It is time to remove vestiges of caloric theory from careful thermodynamic analyses.

Heat effects and work effects are well defined in the *surroundings* of the reactive system (2, 3).¹ Thus, if we wish to know ΔU for a process occurring in a reactive system, we measure q and w in the surroundings and apply eq 1b. The quantity ΔU is found in this way except for a few instances in which we know the internal energy as a function of reactive system variables. Such information about the functional dependence of U comes from auxiliary laws or theories. Thus, in general, if heat and work effects were not well defined in the surroundings, the first law would be useless.

In summary, we have seen that the essence of the first law is that the sum of the heat effect and the work effect is the same regardless of the path between a given initial state and a given final state. Thus, the change in an internal energy function U of the reactive system is defined as in eq 1a in terms of the measurables, the heat effect and the work effect. The parts of the very name of the subject are reminders that we depend on measurement of heat effects (“thermo”) and work effects (“dynamics”).

Thermal Energy

Terminology such as “heat content” and “heat bath” survives, in part, because of a need to describe energy deposited or removed by a heat process. In addition, when mechanical energy is converted by a frictional process within

a reactive system, the temperature rises. In this case, there has, however, been no energy transferred by a heat effect process. A useful and experimentally well-defined concept that describes the outcome of these processes is "thermal energy". Thermal energy is defined operationally as the energy associated with a temperature change in a body that can be a reactive system or a part of the surroundings.² Thermal energy is an energy content, in contrast to a heat effect, which is an energy transfer process. It is useful to call the part of the surroundings that supplies or receives thermal energy, as monitored by its temperature change, a "thermal energy reservoir" or simply a "thermal reservoir". The concept of a thermal reservoir is essential in the global formulation of thermodynamics (2). In most places where "heat" is misused, "thermal energy" is an acceptable substitute.

Adiabatic-Work Formulation of the First Law

Sometimes the first law is initially formulated with reference to adiabatic work. For an adiabatic process, one in which the reactive system is very well insulated from the thermal surroundings and thus no heat effect occurs, we have

$$\Delta U = w_{\text{ad}}$$

where w_{ad} represents an adiabatic work effect. For an adiabatic process between a given initial state and a given final state in the reactive system, experiments would show that w_{ad} is independent of the path and is equal to ΔU . Thus, we appear to have a general way to find ΔU from experiment. Once w_{ad} for a given change in the reactive system is known, then q is found by using

$$w_{\text{ad}} = w + q$$

or

$$q = w_{\text{ad}} - w$$

where w is the work effect for an alternative, nonadiabatic path connecting the same initial and final states of the reactive system.

The adiabatic-work formulation of the first law appears to have the virtue of expressing the presumably less well defined heat effect in terms of well-defined work effects. Problems exist, however, with the generality of the adiabatic-work formulation that are normally not revealed. For example, to connect two states on an isotherm, an alternative, *reversible* adiabatic path is not possible. If such an adiabatic path existed, thermal energy could be converted wholly into mechanical energy for a cyclic process in the reactive system. This outcome would violate the second law. Thus, two adiabats cannot cross, and consequently no reversible adiabatic path exists between states on two different adiabats. The noncrossing of two adiabats is, moreover, the basis for the Carathéodory formulation of the second law (4).

With the incorporation of *irreversible* PV work processes, it is, for example, possible to find an alternative, adiabatic path between two states that lie on an isotherm or that lie on two adiabats. A properly chosen irreversible adiabatic process, such as a pressure drop at constant volume followed by an expansion at constant pressure, carries the system to a new adiabat. To connect two states on an isotherm, at least two adiabatic steps are required, and one must be irreversible. After equations for temperature change and work for an ideal gas are intro-

duced in the section *Adiabatic Processes*, we consider some examples of connecting states with irreversible adiabats. Because an irreversible step is involved in the adiabatic transit between two adiabats or between two states on an isotherm, we find this transit is possible in only one direction—for example, from the state of higher pressure to the state of lower pressure in a gas. However, because $\Delta U = w_{\text{ad}}$, a value for w_{ad} from the initial state to the final state suffices to give ΔU for the backward process as well.

Although we can describe possible alternative adiabatic paths in general terms, it is difficult to do so specifically. One way out of this difficulty is to use the non- PV work effect of a mass dropping in a gravitational field to turn a paddle wheel in a well-insulated reactive system. Thermal energy is produced in the reactive system as a consequence of an irreversible work effect. This thermal energy causes the temperature to rise in the reactive system. An alternative non- PV way to introduce thermal energy by a work effect is by having a measured amount of electrical energy dissipated in a resistor in the reactive system. These two methods of introducing energy into the reactive system by irreversible work effects produce the same outcome in the reactive system as transferring thermal energy by a heat effect from a surrounding, higher temperature thermal reservoir and measuring the temperature change in the thermal reservoir. The paddle-wheel method or electrical heating method is, however, inherently irreversible, whereas the transfer of energy from the surroundings by a heat effect can be made reversible. Thermal energy cannot be removed by the direct reverse of these special work effects. Thermal energy can, however, be removed by contact with a thermal reservoir at a temperature lower than the temperature of the reactive system or by use of a refrigerator.

Is the adiabatic work formulation of the first law conceptually simpler or logically tighter than direct use of a heat effect? The previous paragraphs show that the adiabatic work formulation is roundabout and thus is not simple. To be general, the adiabatic process must be irreversible. Its difficulties are commonly not fully explicated. In contrast, heat effects are as well defined in the surroundings as are work effects. Furthermore, to go through the circuitous path of doing many processes two ways, the adiabatic way and then the desired way, is a complication that no textbook sustains after introducing the adiabatic-work argument. Heat effects are as fundamental to thermodynamics as are work effects. Furthermore, as emphasized in the next section, reversible heat effects are essential to the second law. We see no value in using the adiabatic-work formulation. It is neither logically tighter nor conceptually simpler. Its attractiveness is probably rooted in classical physics where work seems to be a tidier concept than heat.

Reversible Processes

Reversible processes are important in thermodynamics because they involve changes in thermodynamic quantities that can be evaluated by using equations of state of the reactive system. Reversible processes are also the limits of approximating with multistep irreversible processes and are associated with minimum work effects. The work effect is always well defined in terms of the external pressure applied by the surroundings on the reactive system, P_{ext} . For a reversible work

effect, P_{ext} equals P , the pressure in the reactive system, throughout a process. Thus, for reversible processes, $Dw = -PdV$. Although the work effect for reversible processes is expressed in terms of reactive system variables, its value remains dependent on the path, as can be readily shown for the example of an ideal gas. The reversible heat effect, q_{rev} , is especially important because Dq_{rev} is involved in the operational definition of dS through the second law, where

$$dS = Dq_{\text{rev}}/T \quad (2)$$

During reversible heat effects, T equals T_{sur} , comparable to the pressure equality condition for reversible PV work. T_{sur} is the temperature of a surrounding thermal reservoir.

Because of the importance of reversible processes in thermodynamics, there is a tendency to overuse reversible work effects. In two good textbooks, the application of the expression

$$\Delta H = q_P$$

is said to be valid only for a reversible work effect. Were this restriction true, most thermochemistry measurements would be unanalyzable. All the spontaneous chemical reactions that occur in thermochemical studies are irreversible. Such processes carried out in contact with the atmosphere are casually called constant-pressure processes. They are constant pressure as far as the pressure applied by the surroundings, P_{ext} , is concerned. In addition, the pressure in the reactive system, P , equals P_{ext} at the beginning and the end of the process. During the reaction, however, the pressure in the reactive system normally does not equal P_{ext} and is often not well defined. Nor is this condition of reversibility needed. The state function property of the enthalpy function is sufficient. We have

$$\begin{aligned} \Delta H &= \Delta U + P_f V_f - P_i V_i \\ &= \Delta U + P \Delta V \\ &= \Delta U + P_{\text{ext}} \Delta V \\ &= q_P \end{aligned}$$

because $P_{\text{ext}} = P = P_i = P_f$, where i and f stand for initial and final states, respectively. The misleading feature is that the

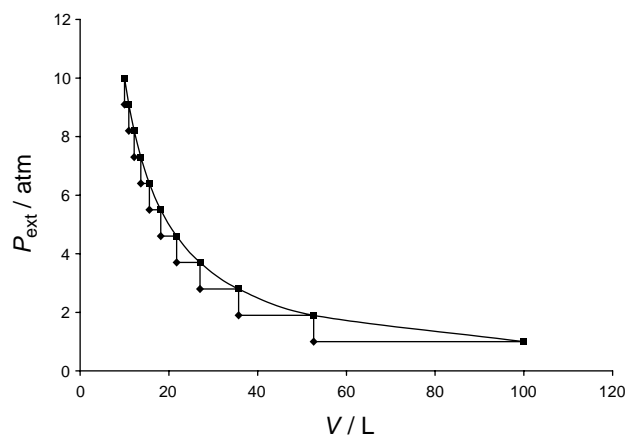


Figure 1. An indicator diagram where P_{ext} , the pressure exerted on the system by the surroundings, is plotted against the volume V of the system. An irreversible path (10 steps) is compared with a reversible path (smooth) for the isothermal expansion of 4.06 mol of an ideal gas at 300 K.

shorthand “constant pressure” is taken too strictly. It does not apply in the reactive system.

The key to understanding this so-called constant-pressure process as well as many other applications in thermodynamics is to emphasize the significance and usefulness of state functions. Alternative paths may be taken in evaluating state functions. Only the initial and final states count.

Irreversible and Reversible Work for Ideal Gases

Before we undertake a full consideration of an operational definition of reversible processes within the context of the first law, it is helpful to consider expressions and outcomes for irreversible work effects for isothermal and adiabatic processes in an ideal gas. Such a discussion will aid the investigation of reversible processes by reference to concrete examples and because reversible processes are limits of multistep irreversible processes.

Only paths for reversible processes that involve equations of state may be drawn on diagrams of state variables such as P and V . If we wish to show work effects in general, including irreversible paths, we must use *indicator diagrams*.³ In these diagrams, P_{ext} is plotted against V . Many textbooks show work effects on PV diagrams rather than $P_{\text{ext}}V$ diagrams. This misunderstanding contributes to an overemphasis on reversible processes.

Isothermal Changes

Figure 1 is an example of a series of irreversible steps related to a reversible isothermal expansion of an ideal gas. The irreversible process is divided into ΔP_{ext} steps of equal size. Each ΔP_{ext} decrease is followed by an isobaric expansion. The integral expression for each step of the irreversible work process for an ideal gas is derived as follows:

$$\begin{aligned} w_{\text{irr}} &= -P_{\text{ext}}(V_2 - V_1) \\ &= -P_2 \left(\frac{nRT}{P_2} - \frac{nRT}{P_1} \right) \\ &= -nRT \left(1 - \frac{P_2}{P_1} \right) \end{aligned} \quad (3)$$

where P_1 and P_2 are the initial and final pressures, respectively, for each step. The other symbols in eq 3 are n for moles, R for the ideal gas constant, and T for the absolute temperature. In addition, we have $\Delta P_{\text{ext}} = P_2 - P_1$. We can recast eq 3 as

$$w_k = -nRT \left(\frac{-\Delta P}{P_k} \right)$$

where $\Delta P = (P_f - P_i)/m$ and $P_k = P_i + k\Delta P$, in which m is the total number of steps and k is the index of the step. The subscripts i and f designate, respectively, the initial and final overall states. For the overall work effect along the irreversible path, we must sum over the w_{irr} contributions for each step to get

$$w = \sum_k nRT \left(\frac{\Delta P}{P_k} \right) \quad (4)$$

The reversible isotherm, for which $P = P_{\text{ext}}$ along the entire path, is a limiting path off which the various irreversible steps hang. For the smooth reversible path in Figure 1,

$$w_{\text{rev}} = nRT \ln (P_f/P_i) \quad (5)$$

a familiar expression for an ideal gas. In Figure 1 it is obvious that the work effect, which is the negative of the area under the path, is numerically smaller for the irreversible path than for the reversible path. Thus, the work along the reversible path is the algebraically minimum work effect done by the gas on the surroundings, a largest negative quantity, for the isothermal expansion.

Analytically, eq 4 becomes eq 5 in the limit of an infinite number of steps. To show this equivalence, we take eq 4 to the limit in which $P_{\text{ext}} = P$ and have

$$w = \sum_k nRT \left(\frac{\Delta P}{P_k} \right) \Rightarrow nRT \int_{P_i}^{P_f} \frac{dP}{P}$$

to give eq 5 when integrated.

An irreversible compression process may consist of a series of steps resting on top of the reversible isotherm. The work effect for the sum of these irreversible steps for an ideal gas is also given by eq 4. The work done by the surroundings on the gas in a compression along the irreversible path is greater than the work done along the reversible path. Thus, the work done along the reversible path is a minimum.

Of course, the heat effect for an irreversible isothermal expansion differs from the heat effect for the reversible isothermal expansion between the same endpoints. Because $|w_{\text{irr}}| < |w_{\text{rev}}|$ and $\Delta U = 0$ for the isothermal expansion of an ideal gas, we also have $|q_{\text{irr}}| < |q_{\text{rev}}|$. For the reversible process the temperature of the gas in this isothermal process remains the same as the temperature of the thermal reservoir, and P_{ext} remains infinitesimally close to P . For the irreversible process, temporary temperature and pressure gradients exist in the gas. For the compression process the directions of the inequalities are reversed.

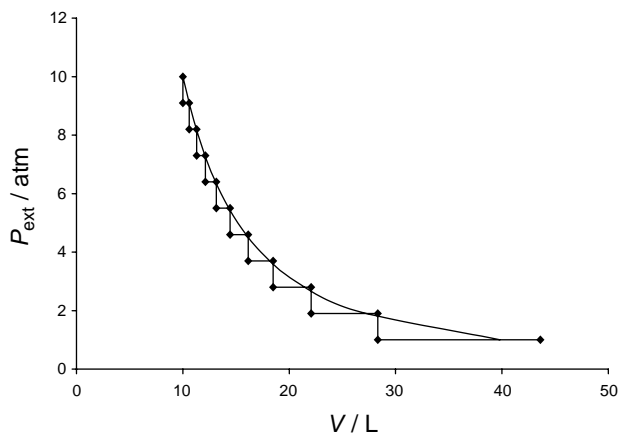


Figure 2. An indicator-diagram comparison of an irreversible path (10 steps) with a reversible path (smooth) for the adiabatic expansion of an ideal gas. See Table 1 for details.

Another instructive formulation of the work effect in an irreversible approximation to a reversible isotherm uses a constant ratio of pressures for successive steps rather than equal changes in pressure. This equal-ratio formulation, which can be expressed in a single equation, is given in the Appendix.

Adiabatic Processes

We also consider the approximation of a series of irreversible steps to a reversible adiabat, for which, of course, there is no heat effect. Figure 2 shows a set of steps, each with the same change ΔP in P_{ext} , approximating a reversible adiabatic expansion. We see that the endpoints of these steps drift away from the reversible adiabat and finish at a final volume that is greater than the final volume of the reversible process. As can be shown from the expressions below, the greater volume occurs because the final temperature is higher for the irreversible process than for the reversible process. Also, the work effect can be shown to be numerically smaller for the irreversible process. The expression for the work effect in each step of the irreversible adiabat is derived as follows.

$$dU = -P_{\text{ext}} dV$$

$$nC_V(T_2 - T_1) = -P_2 \left(\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1} \right)$$

$$(nC_V + nR)T_2 = \left[nC_V + nR \left(\frac{P_2}{P_1} \right) \right] T_1$$

$$T_2 = \frac{T_1 \left[C_V + R \left(\frac{P_2}{P_1} \right) \right]}{C_V + R} \quad (6)$$

where T_1 and P_1 are for the initial state, T_2 and P_2 are for the final state in each step along the expansion path, and C_V is the constant-volume molar heat capacity. The volume at the end of each step is given by

$$V_2 = V_1 \left(\frac{P_1}{P_2} \right) \left[C_V + R \left(\frac{P_2}{P_1} \right) \right] \left(\frac{1}{C_V + R} \right) \quad (7)$$

For expansion along the irreversible path, we have for the work effect in each step

$$w_{\text{irr}} = nC_V(T_2 - T_1)$$

For the full work effect along the path the w_{irr} contributions for each step must be summed.

For a reversible adiabatic process the equation for the adiabat is the familiar expression

$$P_i V_i^\gamma = P_f V_f^\gamma \quad (8)$$

where $\gamma = (C_V + R)/C_V$, P_i and V_i are for the initial state, and P_f and V_f are for the final state. From eq 8 and the ideal gas law, the final temperature, T_f , for the reversible expansion is found to be

$$T_f = T_i \left(\frac{P_f}{P_i} \right)^{R/(C_V + R)} \quad (9)$$

where T_i is the initial temperature. The final volume is given by

$$V_f = V_i \left(\frac{P_i}{P_f} \right)^{C_V/(C_V+R)} \quad (10)$$

The reversible work effect for the process is

$$w_{\text{rev}} = nC_V(T_f - T_i) \quad (11)$$

which is the same expression as for an irreversible step. For a reversible adiabatic process, eq 11 can be recast as

$$w_{\text{rev}} = nC_V T_i \left[\left(\frac{P_f}{P_i} \right)^{R/(C_V+R)} - 1 \right] \quad (12)$$

after substituting eq 9 for T_f .

In the comparison of the reversible and irreversible paths for the adiabatic expansion in Figure 2, as already noted, the final volume for the irreversible path is greater than for the reversible path. A similar, less apparent difference between V_{irr} and V_{rev} holds for each step along the path. If the derivatives, $d(V_2/V_1)/d(P_1/P_2)$, for eqs 7 and 10 are compared, we find that the derivative for eq 10 is always smaller than the derivative of eq 7. Thus, the volume increases less rapidly along the reversible path. This difference in the two volumes increases with the steps along the path. As a consequence, the irreversible adiabatic path drifts away from the reversible adiabatic path. This divergent relationship between the irreversible and reversible paths for the adiabatic path differs from the comparable relationship for the isothermal case.

For the adiabatic process the temperature after each irreversible step is higher than after a comparable reversible change, as can be shown by comparing derivatives of eqs 6 and 9. Thus, ΔT for each irreversible step is smaller than for the corresponding reversible change. The larger ΔT for the reversible step is a consequence of a larger work effect for the reversible expansion. This conclusion holds for the sum of the irreversible steps compared to the reversible process shown in Figure 2. Thus, as for the isothermal process, $|w_{\text{irr}}| < |w_{\text{rev}}|$ for the expansion process.

Figure 3 provides a comparison of the stepwise irreversible compression process with the reversible process starting from the same low-temperature state. The drift of the irreversible path away from the reversible path is more dramatic in the compression process than in the expansion process. This is due to the first, low-temperature step, in which the relative pressure change is the greatest, being the most significant one in the compression process.

Table 1 contains comparisons of the work effect for adiabatic processes during expansion and compression along irreversible paths with two choices of step size and along the reversible path. A monatomic gas with $C_V = 1.5R$ is used for the data in this table and in constructing Figures 2 and 3. As the number of steps increases in an irreversible process, the irreversible work effect approaches the corresponding reversible work effect. Of course, the final volumes and temperatures become closer as well.

It is impractical to show analytically how the sum of the w_{irr} approaches w_{rev} for infinitesimal steps as given in eq 12 even though the equivalence can be shown numerically. If, however, the irreversible adiabatic approximation is expressed

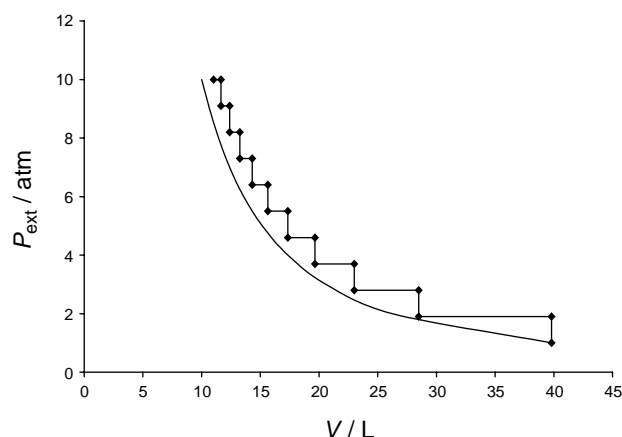


Figure 3. An indicator-diagram comparison of an irreversible path (10 steps) with a reversible path (smooth) for the adiabatic compression of an ideal gas. See Table 1 for details.

Table 1. Work Effects for an Ideal Gas along Irreversible and Reversible Adiabatic Paths

Path	T_i/K	V_i/L	P_i/atm	w/J
<i>Adiabatic Expansion^a</i>				
Irreversible (10 steps)	130.9	43.6	1	-8,564
Irreversible (50 steps)	121.8	40.6	1	-9,025
Reversible (∞ steps)	119.4	39.8	1	-9,143
<i>Adiabatic Compression^b</i>				
Irreversible (10 steps)	330.6	11.0	10	10,692
Irreversible (50 steps)	305.9	10.2	10	9,443
Reversible (∞ steps)	300.0	10.0	10	9,143

^aInitial state: 300.0 K, 10.0 atm, 10.0 L, 4.06 mol. $C_V = 3/2R$.

^bInitial state: 119.4 K, 1.0 atm, 39.8 L, 4.06 mol. $C_V = 3/2R$.

in a series of steps of a fixed ratio of pressures, an analytical expression for w_{irr} can be written. This analytical expression is given in the Appendix, and the corresponding equation for T_f is shown to give eq 9 for the reversible process as the number of steps becomes infinite.

With Figure 2 and related equations in hand, we return to our earlier discussion of the generality of the adiabatic-work formulation of the first law. We first consider an example of taking two irreversible adiabatic steps to go from an initial point on an isotherm to another point on the same isotherm for an ideal gas with $C_V = 1.5R$. Let the initial pressure be 1 atm and the initial temperature be 300 K. Let the final pressure be 0.5 atm and the final temperature be 300 K. In the first irreversible adiabatic step, let the pressure drop to P . The temperature is given with eq 6 as

$$T = 300 \text{ K} [(3/5) + (2/5)(P/1 \text{ atm})] \quad (13)$$

for the first step and as

$$300 \text{ K} = T [(3/5) + (2/5)(0.5 \text{ atm}/P)] \quad (14)$$

for the second step. If eq 13 is substituted into eq 14, we have $300 \text{ K} = 300 \text{ K} [(3/5) + (2/5)(P/1 \text{ atm})][(3/5) + (2/5)(0.5 \text{ atm}/P)]$

When the resulting quadratic equation is solved for P , we obtain 0.2387 atm and 2.095 atm for the two allowed intermediate pressures. For the first path, the external pressure drops to 0.2387 atm, and the gas expands at this pressure and cools to an intermediate temperature, $T = 223.0$ K. Then, the external pressure is increased to 0.5 atm, and the gas contracts at this pressure and warms back to 300 K. For the other path, the external pressure rises to 2.095 atm, and the gas contracts and warms to an intermediate temperature, $T = 557.1$ K. Then, the external pressure drops to 0.5 atm, and the gas expands and cools to 300 K. Along each of the two paths, the two work terms cancel to give $\Delta U = 0$ for the overall isothermal change of the ideal gas. The overall process is irreversible. If the gas is then compressed reversibly to its initial state along the isotherm, the overall change is the conversion of the work effect along this last step into a heat effect. This cyclic process is consistent with the second law. However, the reverse process in which the gas is first expanded reversibly along the isotherm and subjected to adiabatic steps to return to the initial state is impossible. For this impossible process the solutions to the equation obtained from equations like eqs 13 and 14 are imaginary. Such a process would violate the second law.

An alternative adiabatic path between the two states on the isotherm consists of an irreversible expansion (or compression) step followed by a reversible adiabatic compression (or expansion) step. Movement along the reversible adiabat takes the gas back to 300 K. For the first step eqs 6 and 13 apply. For the second step eq 9 is needed. For the conditions of the previous paragraph the equation to be solved is

$$300 \text{ K} = 300 \text{ K} [(3/5) + (2/5)(P/1 \text{ atm})](0.5 \text{ atm}/P)^{2/5}$$

A numerical solution gives the two possible intermediate pressures as 0.2375 atm and 1.7524 atm.

In summary, we have shown that useful expressions can be written for irreversible work effects for an ideal gas expanding or contracting along isothermal and adiabatic paths. The expressions for the isothermal case are not readily available in standard textbooks. To our knowledge, the expressions for the adiabatic case are new. Considering these expressions and their graphical representation helps toward a deeper understanding of the relationship between irreversible processes and reversible processes. The discussion of specific irreversible paths helps put less emphasis on reversible processes in describing work effects and heat effects.

Although we have used the ideal gas for the specific relationships to keep the algebra simple in this presentation, this simplification is not necessary. Other equations of state such as the van der Waals or virial expressions could also be used. Numerical methods may then have to be applied in most cases. Also, the step size in the irreversible processes need not be uniform nor need the gas be monatomic.

Reversible Processes and the First Law

In our discussion to this point, we have assumed familiarity with the concept of reversibility and have compared work effects for irreversible and reversible paths. We now consider reversibility itself and show how it is operationally defined within the context of the first law, as it must be. In textbooks it is common to say that a reversible process goes through a

succession of equilibrium states. Then, it turns out that equilibrium is defined in terms of the second law, for which a reversible heat effect is needed for evaluating dS according to eq 2. Clearly, a definition of a reversible heat effect in terms of equilibrium states is circular and not operational.

An operational definition of a reversible process in first-law terms is as follows. For a reversible process, traversing the same path in reverse not only restores the system of interest to its original state (as defined by variables such as T , P , n , etc.) but also restores all parts of the interacting surroundings to their initial conditions (as defined by similar variables). A reversible process does not involve reverse steps, but certifying a process as reversible involves consideration of the reverse of the process. The adjective "reversible" reminds us of this test condition. A definition similar to this one for reversible processes is given by Zemansky (5), as well as by other authors (7), but the consequences of this definition are not fully worked out.

To apply the test of a reversible process, it is often sufficient to consider the work and heat effects for the two directions. If $\Delta U_f = q_f + w_f$ for the forward process (f = forward) and $\Delta U_b = q_b + w_b$ for the reverse process (b = back), then for a reversible process $w_b = -w_f$ and $q_b = -q_f$ and necessarily $\Delta U_f = -\Delta U_b$.⁴ Equivalently, $w_b = -w_f$ guarantees $q_b = -q_f$ under these conditions. This test for reversibility depends only on first law concepts.

First, we relate the first law test of reversible processes to our prior investigation of isothermal expansions and compressions. For this process the reactive system is in good thermal contact with a large thermal reservoir at temperature T . For expansion along the reversible isotherm in Figure 1, $w_{f,rev}$ is the negative of the area under the curve. For the compression along the same isotherm as in Figure 1, $w_{b,rev}$ is the area under the same curve. Thus, $w_{f,rev} = -w_{b,rev}$. Also, $\Delta U_f = -\Delta U_b$ because U is a state function. Consequently,

$$q_{f,rev} + w_{f,rev} = -q_{b,rev} - w_{b,rev}$$

and

$$q_{f,rev} = -q_{b,rev}$$

Because the two work effects cancel and the two heat effects cancel for the two directions, no net change occurs in the surroundings for the cycle of going from the initial state to the final state and back to the initial state. Thus, we have confirmed that the path from the initial state to the final state along the isotherm, for which $P = P_{ext}$, is a reversible path.

For an isothermal forward-and-back process consisting of an irreversible stepwise expansion and an irreversible stepwise compression, we see immediately from Figure 1 and its counterpart for the compression process that $w_{f,irr} \neq -w_{b,irr}$. In fact, $|w_{f,irr}| < |w_{b,irr}|$. Similarly, $|q_{f,irr}| < |q_{b,irr}|$. Thus, net changes occur in the surroundings in the forward-and-back process as is characteristic of an irreversible process.

For the reversible adiabatic process applying the first law condition depends only on considering w . Figures 2 and 3 show, for example, that $w_{f,rev}$ is the negative of $w_{b,rev}$. Because $w_{f,rev} = -w_{b,rev}$ and $q = 0$, the condition of no net change in the surroundings is met for the forward-and-back process.

As is shown in most physical chemistry textbooks, a generalized reversible process can be approached with an infinite number of tiny, joined Carnot (reversible) cycles. Thus the analysis of isotherms and adiabats suffices to describe

all reversible processes and to enable the formulation of the entropy function in eq 2.

Despite the generalization to all reversible processes in the previous paragraph, we consider one other example of the direct application of the first law test for reversibility. This discussion brings out a more subtle consideration regarding restoration of the surroundings. Consider the warming of a reactive system initially at T_1 by bringing it in contact with a thermal reservoir at the higher temperature of T_2 . To see that this transfer of thermal energy is irreversible, we consider returning the reactive system to its initial temperature by bringing it in contact with another thermal reservoir at the lower temperature of T_1 . Although the cycle returns the reactive system to its initial state and $q_f = -q_b$, the surroundings have been altered. Thus, the criterion of $q_f = -q_b$ is met but is not sufficient. The surroundings have not been restored to their original state. The thermal reservoir at T_2 has lost energy; the thermal reservoir at a different temperature T_1 has gained the amount of energy.⁵ We conclude that the condition $w_b = -w_f$ or $q_b = -q_f$ is necessary to guarantee that a process is reversible, but it may not be sufficient. The stronger criterion is that the surroundings be unchanged in any way at the end of the forward-and-back process.

Of course, a reactive system may be warmed or cooled by a reversible process. To do so we must have an infinite number of thermal reservoirs at slightly different temperatures along the T_1 -to- T_2 temperature interval. From each reservoir an infinitesimal amount of thermal energy is transferred into the reactive system. The same succession of reservoirs would be used for the cooling process. The temperatures of the reactive system and the thermal reservoirs are the same at each infinitesimal step throughout the process, that is, $T = T_{\text{sur}}$ for a reversible process. At the end of the forward-and-back event, all of the infinite number of thermal reservoirs are restored to their initial states as required for a reversible process.

In this section, we have seen how reversible processes can be defined operationally in terms of first-law criteria. Thus, reversible processes are ones in which the surroundings are left unchanged when the reverse of the process is carried out. In particular, Dq_{rev} is defined in first-law terms for use in eq 2 for the second law.

Conclusion

The first law of thermodynamics is expressed in terms of heat effects and work effects, which are operationally defined in the surroundings. Formulating the first law in terms of adiabatic work is neither simpler nor logically stronger than the traditional formulation in terms of heat and work effects. Algebraic expressions can be written for stepwise irreversible isothermal processes and stepwise irreversible adiabatic processes. As the steps in an irreversible adiabatic process are made larger, the endpoints of the irreversible steps drift farther away from the reversible adiabat. Evaluation of these expressions for increasingly small steps shows how the magnitude of the work effect for the irreversible path approaches the value for the reversible path. Reversible processes must be defined in first-law terms as a basis for using reversible processes to develop the second law, which is expressed in terms of $dS = Dq_{\text{rev}}/T$. Reversible processes are ones in which the

surroundings are unchanged in a forward-and-back process that also restores the reactive system to its initial state.

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Notes

1. For a full exploration of heat and work effects, including a discussion of how they are operationally defined in the surroundings, see ref 3. In the present paper, PV work is defined for the system and piston at rest at the beginning and end of a process.
2. Strictly speaking, we must distinguish between thermal energies associated with constant-volume and constant-pressure heat capacities in both reactive systems and thermal reservoirs.
3. The term *indicator diagram* appears in ref 5, but the proper association with P_{ext} appears in reference 6.
4. These w and q conditions for reversible processes are also important in developing the consequences of the second law from a study of heat engines.
5. Cooling from T_2 to T_1 by a reversible process would not give fully restored surroundings.

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Appendix

If the series of steps in an irreversible process involves fixed ratios of pressures rather than fixed pressure differences, then single analytical expressions can be derived for the overall processes.

Isothermal Process. For a series of m isothermal steps with a fixed ratio of pressures for each step, we have

$$P_k = P_i \left(\frac{P_f}{P_i} \right)^{k/m}$$

for the pressure P_k after the k th step, where P_f and P_i are the final and initial pressures, respectively. Because

$$P_{k+1} = P_k \left(\frac{P_f}{P_i} \right)^{1/m}$$

each step has the same work effect. To get the total work ef-

fect we use eq 3 and multiply by m to obtain

$$w = -nRTm \left[1 - \left(\frac{P_f}{P_i} \right)^{1/m} \right]$$

The graphical presentation is similar to Figure 1 except that the steps have equal pressure ratios, and the work effect area under each step is equal. With l'Hôpital's rule, one can show that this expression gives eq 5 as m goes to infinity. Before applying l'Hôpital's rule express the m factor as $1/m$ in the denominator. The derivative

$$d(a^{1/m})/dm = -(1/m^2)a^{1/m} \ln a$$

Adiabatic Expansion. For an irreversible adiabatic process in which the steps consist of equal pressure ratios, we have from eq 6

$$T_{k+1} = \frac{T_k}{a+1} \left[a + \left(\frac{P_f}{P_i} \right)^{1/m} \right] \quad (\text{A1})$$

where $a = C_V/R$. This temperature ratio is independent of k . Thus, after m steps, we have

$$T_f = T_i \left[\frac{a + \left(\frac{P_f}{P_i} \right)^{1/m}}{a+1} \right]^m$$

From this expression for the ratio of initial and final temperatures and eq 11, the work effect is calculated. The graphical presentation is similar to Figure 3 except that the steps have equal pressure ratios and the drift away from the reversible adiabatic curve is more evident from the outset.

We can show that eq A1 becomes eq 9 for the reversible process as m goes to infinity. To simplify the algebra let $P_f/P_i = b$. Then eq A1 becomes

$$T_f = T_i \left[\frac{a + b^{1/m}}{a+1} \right]^m \quad (\text{A2})$$

and eq 9 becomes

$$T_f = T_i(b)^{1/(a+1)}$$

From the exponential term in the brackets in eq A2, we have a series approximation

$$b^{1/m} = e^{(\ln b)/m} \approx 1 + (\ln b)/m + [(\ln b)/m]^2/2 + \dots$$

For large m we retain only the linear term. Then, eq A2 reduces to

$$T_f \approx T_i \left[\frac{a+1 + \frac{\ln b}{m}}{a+1} \right]^m = T_i \left[1 + \frac{\ln b}{m(a+1)} \right]^m \quad (\text{A3})$$

From calculus we know that

$$\lim_{m \rightarrow \infty} \left(1 + \frac{k}{m} \right)^m \rightarrow e^k$$

Thus, as $m \rightarrow \infty$, eq A3 becomes

$$\begin{aligned} T_f &= T_i \exp[(\ln b)/(a+1)] = T_i b^{1/(a+1)} \\ &= T_i (P_f/P_i)^{1/(a+1)} \end{aligned} \quad (\text{A4})$$

Equation A4 is the same as eq 9. Thus, for an infinite number of steps, eq A2, which applies to the adiabatic expansion when the pressure change in each step is an equal ratio of pressures, becomes the equation for the reversible adiabatic expansion.