

Closed system

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Part of a book on [Thermodynamics](#)

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Act Two: Entropy meets volume in closed systems, producing a child—pressure.

The child coincides with pressure in mechanics, which is defined as force per unit area.

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Closed system is characterized by function $S(U,V)$

We have described [a classification of systems](#): isolated systems, thermal systems, closed systems, and open systems. This scheme classifies a system not by the content of the system, but by the interaction between the system and the surroundings. This chapter is devoted to closed systems.

By a *closed system* we mean a part of the world that interacts with the rest of the world by transferring energy and volume, but not matter. The closed system can have multiple species of molecules and multiple phases.

Now enters a second supporting role—*volume*. In thermodynamics, energy and volume play analogous roles.

Cylinder and piston. It helps to have an experiment in mind. Consider a fixed number of H_2O molecules, sealed in a cylinder by a piston. Some of the H_2O molecules form water, and others form steam. The water and steam together constitute a closed system.



Fire and weight. The closed system is in contact with a *thermomechanical environment*: a fire under the cylinder, and a weight over the piston.

Closed system has two independent variables: volume and energy. The two variables, V and U , can vary independently. Volume V is varied by sliding the piston. When V is fixed by jamming the piston, the weight does not affect the H_2O molecules in the cylinder, and U can vary by the fire.

When the closed system—i.e., the combined water and steam in the cylinder—is our focus, we will track V and U . The specific method to vary V and U do not concern us. For example, instead of fire, we can submerge a resistor in the water, and pass an electric current in the resistor to add energy to the H_2O molecules.

A closed system is a family of isolated systems. We fix energy U and volume V by insulating the cylinder and jamming the piston. When U and V are fixed, the closed system becomes an [isolated system](#). The isolated system flips among a set of quantum states. Denote the number of quantum states of this isolated system by $\Omega(U, V)$.

When U and V vary, the function $\Omega(U, V)$ characterizes the closed system as a family of isolated systems. Each member in the family is an isolated system, specified by fixed values of U and V .

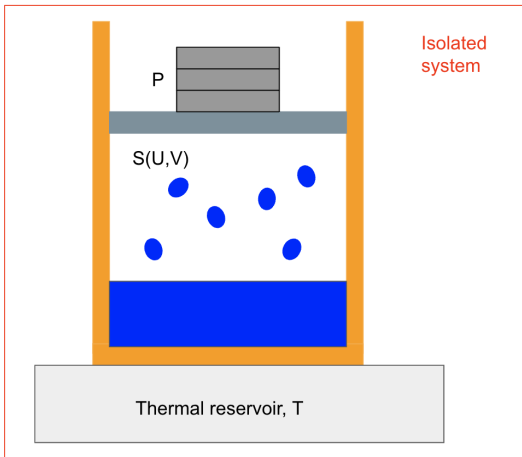
Recall the definition of [entropy](#). The entropy of an isolated system is the logarithm of the number of quantum states of the isolated system. Write

$$S(U, V) = \log \Omega(U, V)$$

Entropy meets energy and volume in the closed system.

Closed system in thermomechanical environment

Look again at the fluid sealed in a cylinder by a piston. The closed system is in thermal contact with a [thermal reservoir](#) of a fixed temperature T . By replacing the fire with a thermal reservoir, we make the analysis explicit. Placed above the piston is a weight, which exerts on the piston a fixed force PA , where A is the base area of the piston, and P is the applied force per area exerted by the weight. When the piston is at height Z , the volume of the cylinder is $V = AZ$, and the potential energy of the weight is $PAZ = PV$.



For the closed system enclosed by the cylinder and piston, the thermal reservoir and the weight together provide a *thermomechanical environment*, characterized by a fixed temperature T and a fixed pressure P . We next analyze this experiment using the [basic algorithm of thermodynamics](#).

Construct an isolated system with internal variables. Model this experiment by an isolated system of three parts: the fluid enclosed in the cylinder and piston, the weight above the piston, and the thermal reservoir.

The energy of the isolated system is the sum of the energies of its three parts:

$$U_{\text{iso}} = U + PV + U_R$$

where U the energy of the closed system, PV the potential energy of the weight, and U_R the thermal reservoir.

The isolated system conserves energy, so that U_{iso} is constant. The isolated system has two independent internal variables: U and V . The energy U_R of the thermal reservoir is a dependent variable: $U_R = U_{\text{iso}} - U - PV$.

Find subset entropy of the isolated system as a function of independent internal variables. The subset entropy of the isolated system is the sum of the entropies of its three parts:

$$S_{\text{iso}} = S(U, V) + S_{\text{weight}} + S_{\text{R}}(U_{\text{R}})$$

where $S(U, V)$ is the entropy of the closed system, S_{weight} is the entropy of the weight, and $S_{\text{R}}(U_{\text{R}})$ is the entropy of the thermal reservoir. Because the temperature of the thermal reservoir, T , is constant, $S_{\text{R}}(U_{\text{R}})$ is a linear function, so that

$$S_{\text{R}}(U_{\text{R}}) = S_{\text{R}}(U_{\text{iso}}) - (U + PV)/T$$

Maximize subset entropy to equilibrate. The entropy S_{weight} of the weight is constant. Because U_{iso} is constant, $S_{\text{R}}(U_{\text{iso}})$ is also constant. A change in the subset entropy of the isolated system is the same as a change in the following quantity:

$$S(U, V) - (U + PV)/T$$

In this function, U and V are independent variables of the closed system, but T and P are constant, set by the thermal reservoir and the weight.

Maximizing a function $S_{\text{iso}}(U, V)$ requires that

$$\partial S(U, V)/\partial U = 1/T$$

$$\partial S(U, V)/\partial V = P/T$$

Increase subset entropy to undergo an irreversible process. Any actual process of an isolated system is irreversible. When the two internal variables change by dU and dV , the subset entropy of the isolated system, S_{iso} , must increase, so that

$$dS - (dU + PdV)/T > 0$$

Replacing dS with the identity $dS(U, V) = (\partial S(U, V)/\partial U)dU + (\partial S(U, V)/\partial V)dV$, we obtain that

$$(\partial S(U, V)/\partial U - 1/T)dU + (\partial S(U, V)/\partial V - P/T)dV > 0$$

This inequality holds for arbitrary combinations of dU and dV . When $dV = 0$, the inequality becomes

$$(\partial S(U, V)/\partial U - 1/T)dU > 0$$

When $dU = 0$, the inequality becomes

$$(\partial S(U, V)/\partial V - P/T)dV > 0$$

The irreversibility is caused by the transfer of energy between the fluid in the cylinder and the thermal reservoir, and by the friction between the piston and the wall of the cylinder. We have studied the former, and let us examine the latter.

When the isolated system is in thermal equilibrium, the subset entropy does not change when the energy U changes, so that $\partial S(U,V)/\partial U = 1/T$. In the isothermal process, the entropy inequality becomes that

$$(\partial S(U,V)/\partial V - P/T)dV > 0$$

This inequality recovers our experience. When the piston moves up, $dV > 0$, the pressure in the cylinder must exceed the pressure due to the weight, $\partial S(U,V)/\partial V > P$. The opposite is true when the piston moves down. The difference between the two pressures is caused by the friction between the piston and the wall of the cylinder.

As an idealization, a reversible process of an isolated system keeps the subset entropy constant. The conditions of reversibility are obtained by replacing all the entropy inequality with equality:

$$(\partial S(U,V)/\partial U - 1/T)dU + (\partial S(U,V)/\partial V - P/T)dV = 0$$

This inequality holds for independent changes dU and dV . Thus, a reversible process requires that

$$\begin{aligned}\partial S(U,V)/\partial U &= 1/T \\ \partial S(U,V)/\partial V &= P/T\end{aligned}$$

These conditions of reversibility coincide with those of equilibrium. In practice, a reversible process represents a limiting case when the difference in temperature and the difference in pressure between the closed system and the thermomechanical environment are negligibly small.

Tweet [Apply the basic algorithm of thermodynamics to a closed system](#)

Definition of pressure

The above analysis identifies the significance of the two partial derivatives, $\partial S(U,V)/\partial U$ and $\partial S(U,V)/\partial V$. Nature works well with these derivatives, but humans like to call them by some names. Let us examine the conditions of equilibrium:

$$\begin{aligned}\partial S(U,V)/\partial U &= 1/T \\ \partial S(U,V)/\partial V &= P/T\end{aligned}$$

The first equation recovers the condition of thermal equilibrium. The left hand side is associated with the closed system, and the right hand side is associated with the thermal reservoir. In thermal equilibrium, the closed system and the thermal reservoir have the same temperature.

The second condition is the condition of mechanical equilibrium, and is new. The left hand side is associated with the closed system, and the right hand side is associated with the thermal reservoir and the weight. In thermal equilibrium, the temperature in the closed system equals that of the thermal reservoir. Rewrite the second equation as

$$T\partial S(U,V)/\partial V = P$$

To interpret this condition of mechanical equilibrium, we define the quantity $T\partial S(U,V)/\partial V$ as the pressure in the closed system. In mechanical equilibrium, the pressure in the closed system equals the pressure applied by the weight.

When the isolated system is in equilibrium, T is the temperature for both the closed system and the thermal reservoir, and P is the pressure for both the closed system and the pressure exerted by the weight on the piston. The two equations interpret the two partial derivatives of the function $S(U,V)$ of the closed system.

Experimental determination of the function $S(U,V)$ of a closed system

For a function of two variables, $S(U,V)$, recall a fact of calculus:

$$dS(U,V) = (\partial S(U,V)/\partial U)dU + (\partial S(U,V)/\partial V)dV$$

Write

$$dS = (1/T)dU + (P/T)dV$$

This equation connects five properties of a closed system: U , V , S , T , P .

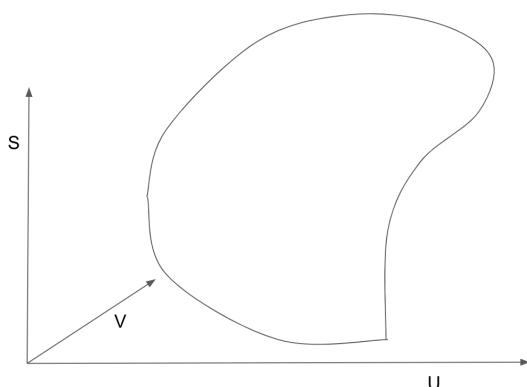
All quantities in the above equation belong to the closed system. This equation relates the characteristic function $S(U,V)$ to measurable quantities, U , V , P , T . By changing the energy and volume, we can measure the function $S(U,V)$. In integrating entropy, recall that entropy is absolute: $S(U,V) = 0$ as $T(U,V) \rightarrow 0$.

The function $S(U,V)$ characterizes the closed system as a family of isolated systems. Thus, we can experimentally count the number of quantum states for each member isolated system in the family. For example, steam tables list values of [entropy](#) of H_2O molecules in various states.

Energy-volume-entropy space

Each of the three properties—energy, volume, and entropy—is an extensive property. Together they form a three-dimensional vector space without inner product. The significance of the energy-volume-entropy space was recognized by Gibbs (1873).

Drawing a three-dimensional vector space on a piece of paper is impossible, but the picture is so suggestive that we fake. We draw energy U and volume V as two horizontal axes. We draw entropy S as the vertical axis. Although being vertical is meaningless in a vector space without inner product, we fake.



Function $S(U,V)$. Note the following features of the surface $S(U,V)$ common to many closed systems.

1. Because energy is relative to an arbitrary reference, the surface $S(U,V)$ can translate in the direction of energy by an arbitrary amount without affecting the behavior of the closed system.
2. Because entropy is absolute, the surface starts at $S = 0$, and cannot be translated up and down.
3. Volume is also absolute and positive, and the surface cannot translate in the direction of the V axis.
4. The more energy and volume, the more quantum states. Thus, $\Omega(U,V)$ is an increasing function with respect to both U and V . Because logarithm is an increasing function, $S(U,V)$ is also an increasing function. That is, the slopes $\partial S(U,V)/\partial U$ and $\partial S(U,V)/\partial V$ are positive.
5. When a plane is tangent to the surface $S(U,V)$ at a point, the two slopes of the tangent plane represent $1/T$ and P/T .
6. For each fixed V , as S approaches zero, $S(U,V)$ is a curve that approaches the U axis vertically. That is, $\partial S(U,V)/\partial U$ approaches infinity as S approaches zero.
7. For the time being, $S(U,V)$ is taken to be a *convex function*. Nonconvex $S(U,V)$ surfaces correspond to phase transition. See [theory of pure substance](#).

Subset entropy of the isolated system

Now return to the isolated system of three parts: the fluid in the cylinder, the thermal reservoir, and the constant weight. Up to an additive constant, the subset entropy of this isolated system is

$$S(U,V) - (U + PV)/T$$

The two independent variables are the energy U and volume V of the fluid in the cylinder. The term $S(U,V)$ is the surface of the closed system, and is a curved surface in the energy-volume-entropy space. The term $(U + PV)/T$ comes from the change in entropy of the thermal reservoir, and is a plane in the energy-volume-entropy space. The slope of the plane with respect to the energy axis is $1/T$, and the slope of the plane with respect to the volume axis is P/T .

A given pair of values of U and V corresponds to a line parallel to the entropy axis. The function $S(U,V) - (U + PV)/T$ is the distance between the curved surface $S(U,V)$ and the plane $S = (U + PV)/T$. The subset entropy $S(U,V) - (U + PV)/T$ maximizes when a tangent plane of $S(U,V)$ parallels the plane $S = (U + PV)/T$.

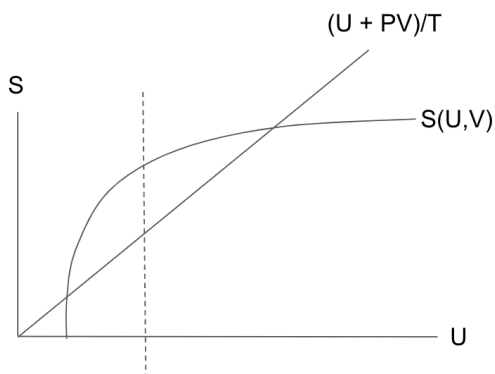
This picture corresponds to facts of calculus:

$$\partial S(U,V)/\partial U = 1/T$$

$$\partial S(U,V)/\partial V = P/T$$

These conditions reproduce what we have obtained before.

A three-dimensional figure drawn on a plane is confusing. Here we fix V and draw a figure on the energy-entropy plane.



Enthalpy

A fluid (e.g., a steam-water mixture) is sealed in a cylinder by a piston. A weight is placed above the piston, and a fire is in thermal contact with the fluid.



The fluid sealed in the cylinder is a closed system. The closed system interacts with its surroundings in two ways: thermal contact with the fire, and pressure from the weight. States of the closed system are specified by two independent properties: volume V and energy U .

The fluid pushes the piston up, and the weight pushes the piston down. In a reversible process, the piston slides without friction. The balance of forces requires that the pressure in the fluid equals the pressure applied by the weight.

Process under constant pressure. Assume that placed on the piston is a *constant weight*. Let P be the pressure applied by weight to the piston, and A be the base area of the piston. Thus, the weight is PA . Because A is constant, a constant weight applies a constant pressure. When the weight is at a height Z , the volume of the fluid is $V = AZ$, and the potential energy of the constant weight is $PAZ = PV$.

The fluid and the weight together constitute a [thermal system](#). The thermal system interacts with its surroundings in only one way: transfers energy by thermal contact with the fire. States of the thermal system are specified by a single variable: the energy of the thermal system. The energy of the thermal system is the sum of the energy of the fluid, U , and the potential energy of the weight, PV . Denote the energy of this thermal system by

$$H = U + PV$$

The quantity H relates to U , P , V , which are functions of state. Consequently, H is also a function of state, called the *enthalpy* of the closed system. Enthalpy is an extensive property. Because energy U is a relative property, so is enthalpy. Enthalpy was introduced by Gibbs (1875).

Thus, the same experimental setup can be viewed as a closed system or a thermal system, depending on how we partition parts of the setup into a system and its surroundings. If the fluid is viewed as a closed system, H is the enthalpy of the closed system. If the fluid and weight together constitute a thermal system, H is the energy of the thermal system.

Thermal capacity at constant volume

A closed system under constant volume is a [thermal system](#). The energy gained by this thermal system from the surroundings is denoted by $U(T,V)$. For a thermal system, [thermal capacity](#) is defined as energy gained per unit increase in temperature. For a closed system under constant volume, this definition becomes that

$$C_V = \partial U(T,V)/\partial T$$

The subscript V indicates that the volume is fixed. Thermal capacity at constant volume is a function of state, $C_V(T,V)$.

Here we have chosen (T,V) as independent variables. For further discussion of this choice, see a chapter on [change of variable](#).

Thermal capacity at constant pressure

Picture a closed system under constant pressure by a cylinder-piston setup enclosing a fixed amount of fluid, subject to a constant weight, and placed over a fire.

The fixed amount of fluid in the cylinder and the constant weight above the piston together constitute a thermal system. The energy of this thermal system is the sum of the thermal energy of the fluid and the potential energy of the weight, $U + PV$. This sum is called the *enthalpy* of the closed system: $H = U + PV$.

For a closed system under constant pressure, the definition for thermal capacity becomes that

$$C_P = \partial H(T,P)/\partial T$$

The subscript P indicates that the pressure is fixed. Thermal capacity at constant pressure is a function of state, $C_P(T,P)$. Here we have chosen (T,P) as independent variables.

Exercise. Give a physical intervention for the inequality $C_P > C_V$.

Exercise. For an ideal gas, show that $C_P = C_V + Nk$.