Heat
&
Thermodynamics

Concepts in Thermal Physics
   — Stephen J. Blundell & Katherine M. Blundell

Chapter 11, 12, 13, 14, 16, 18.

System and surroundings

A thermodynamic system is the part of the universe we are considering. Everything else is referred to as the surroundings.
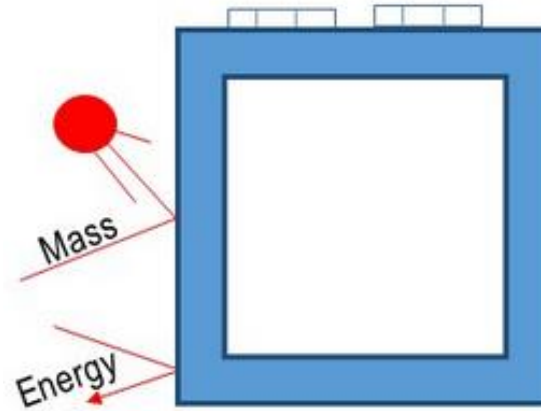
We are free to define the 'system' anyway we chose. However, how we define it may determine whether we can successfully apply thermodynamics.

A thermodynamic system includes anything whose thermodynamic properties are of interest.

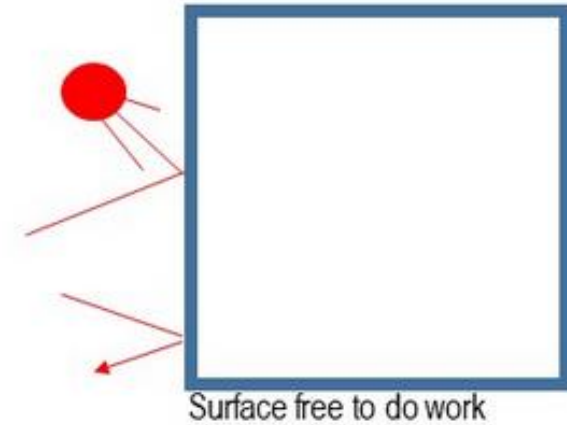Surroundings

Piston

Boundary

Surroundings

System

Surroundings

System

Surroundings

Surroundings

Boundary

(a)

(b)
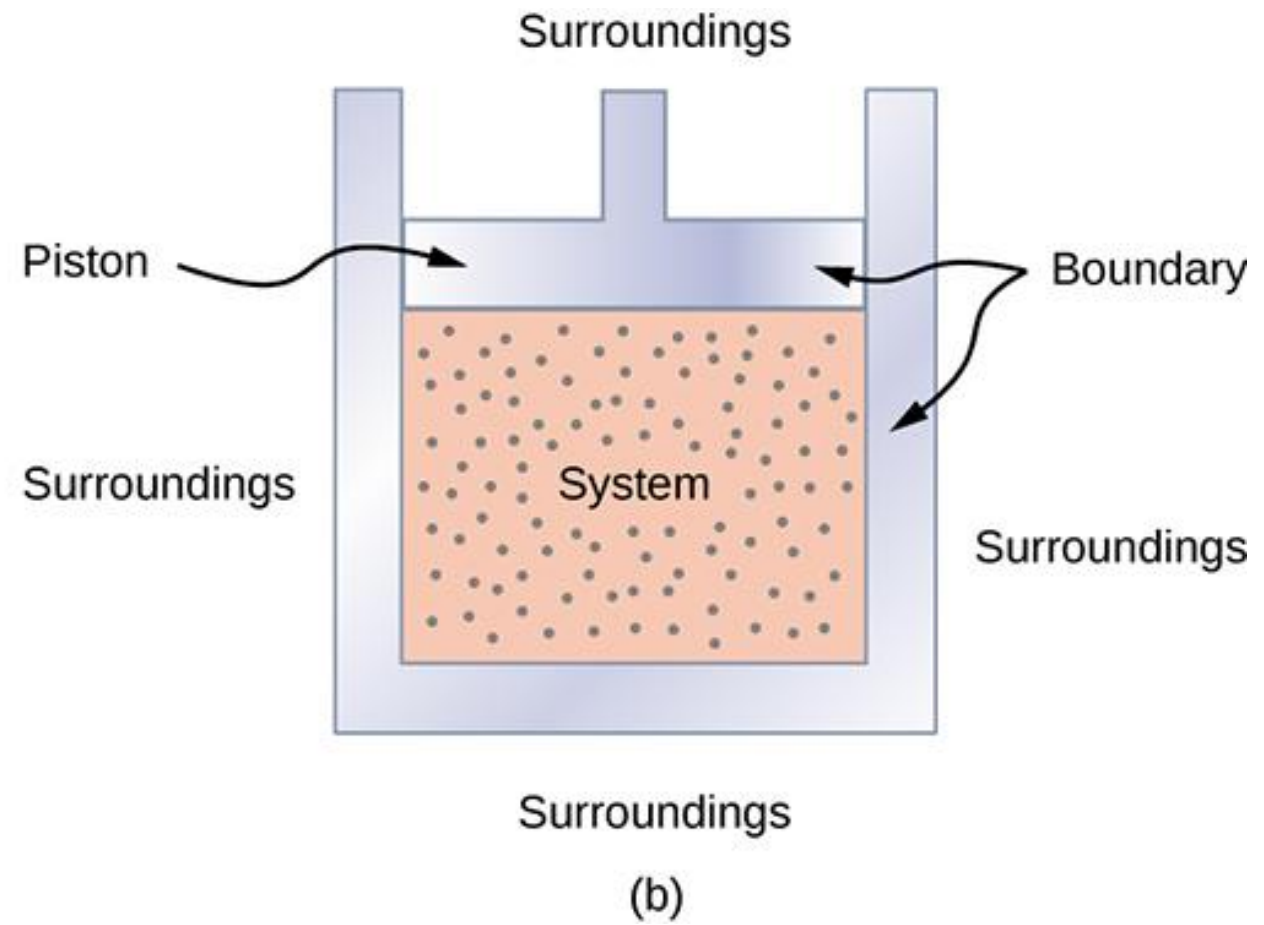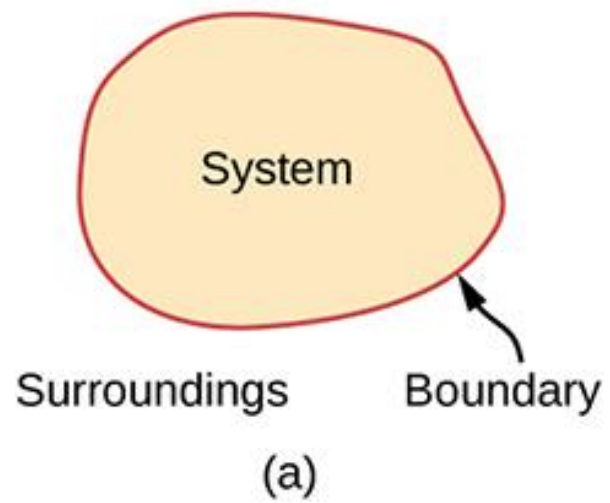
Four kinds of 'systems'

Isolated System

Adiabatic System

Surface free to do work

Closed System

Open System

Mass

Energy
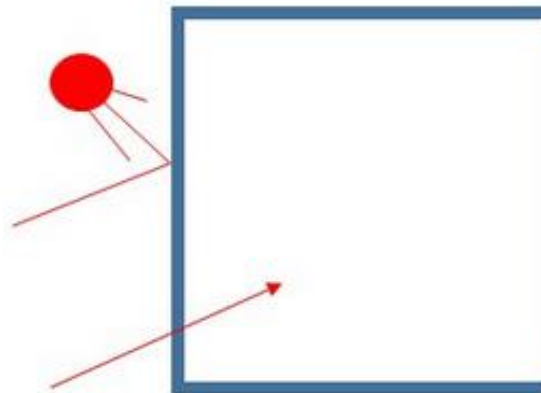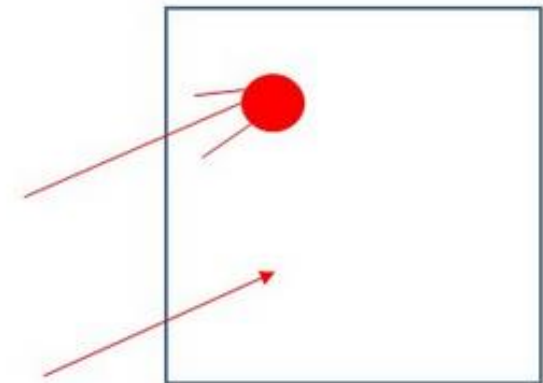
State of a system is the condition of a system.

State variables: P, V, n, T

For ideal gas $\qquad\qquad PV = nRT$

Thermodynamic process

A thermodynamic process is a passage of a thermodynamic system from an initial to a final state.

$P_1 V_1 T_1$

Process
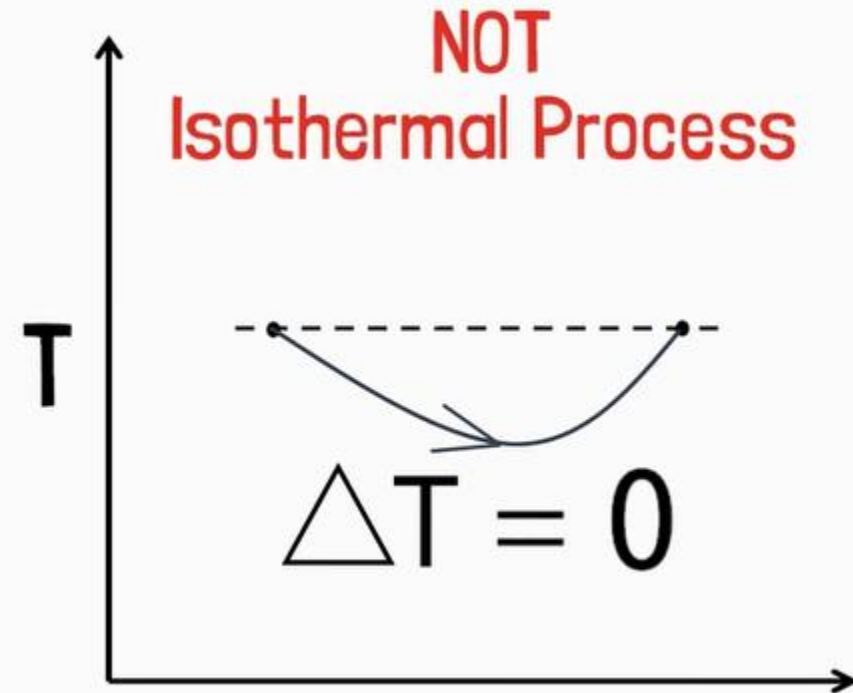Process brings change in State of the System

$P_2 V_2 T_2$

Thermodynamic process

- Isobaric: pressure of the system remains constant

- Isochoric: the volume of the system remains constant

- Isothermal: the temperature of the system remains constant

- Adiabatic: the amount of heat of the system remains constant

Isothermal Process

It is a process in which
Temprature remains Constant throughout the process.

T = Constant

Isothermal Process

T

T $\longrightarrow$ T

T = Constant

$\triangle T = 0$

NOT Isothermal Process

T

$\triangle T = 0$

P

V

P = Constant

Isobaric Process

V = Constant

Isochoric Process

P

V

Isothermal Process and Adiabatic Process

P

V
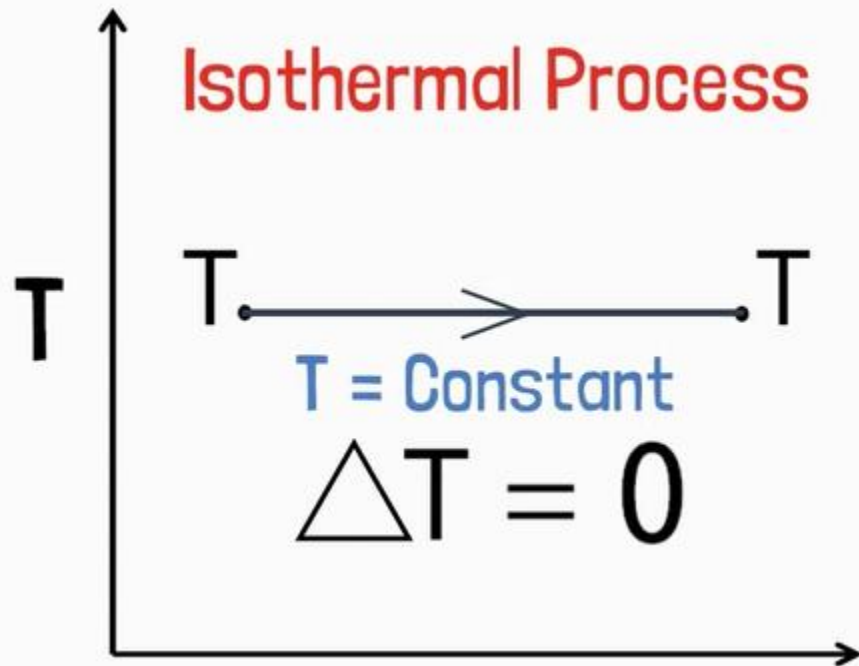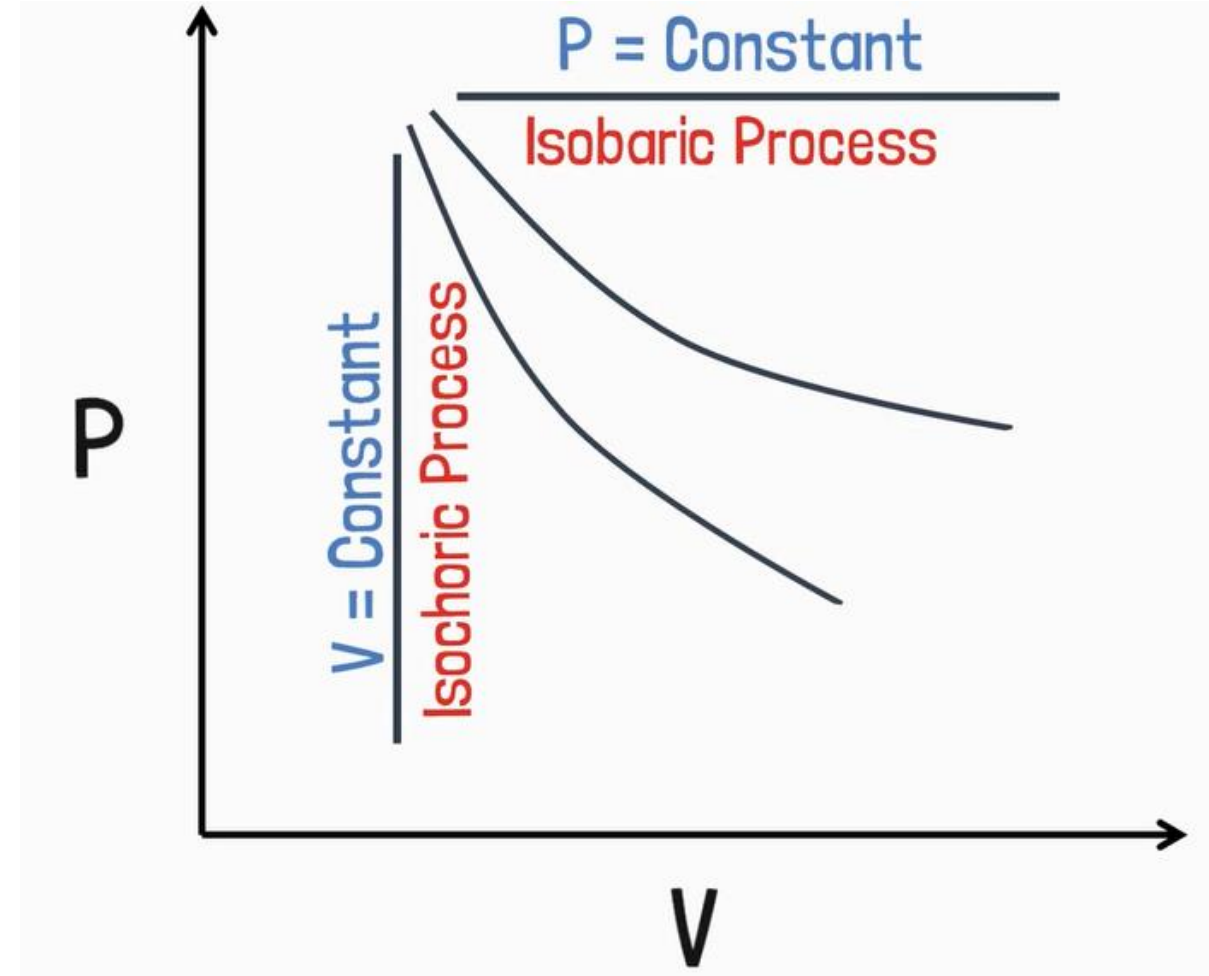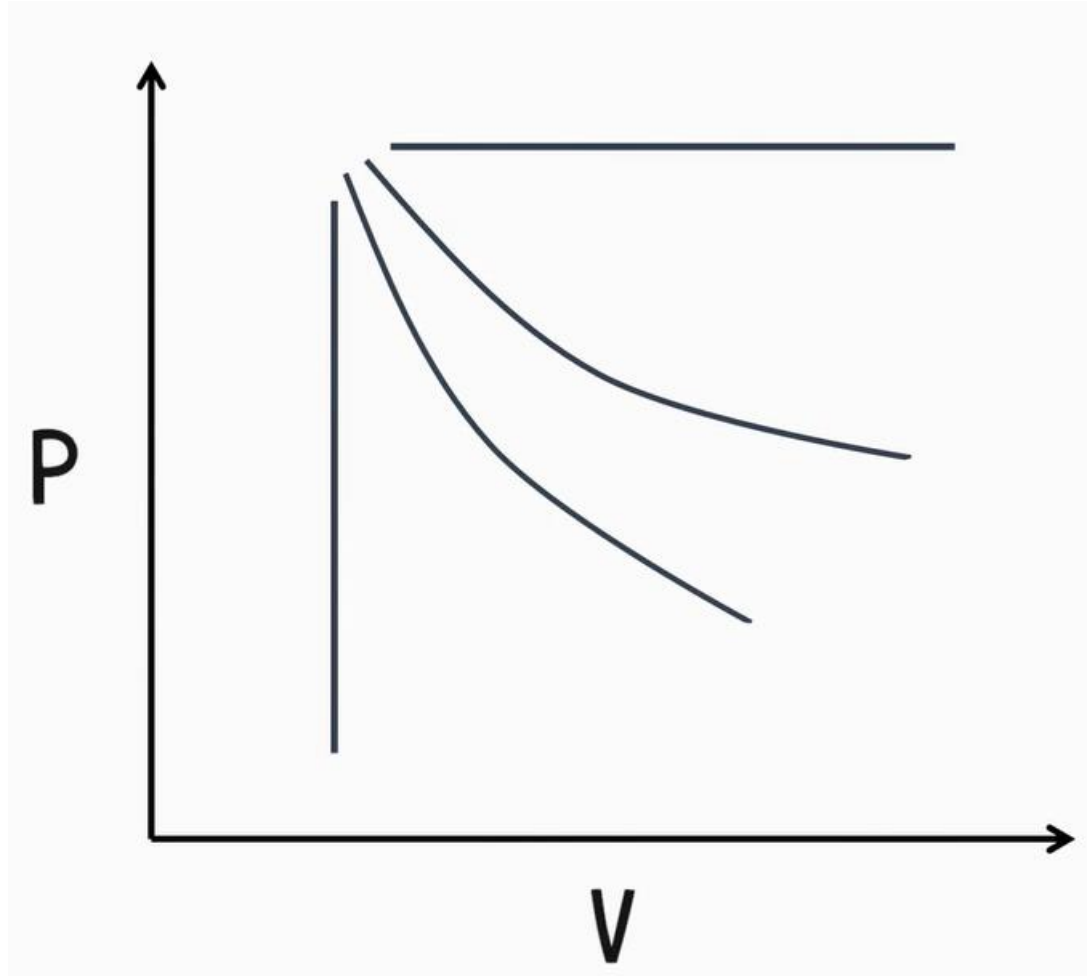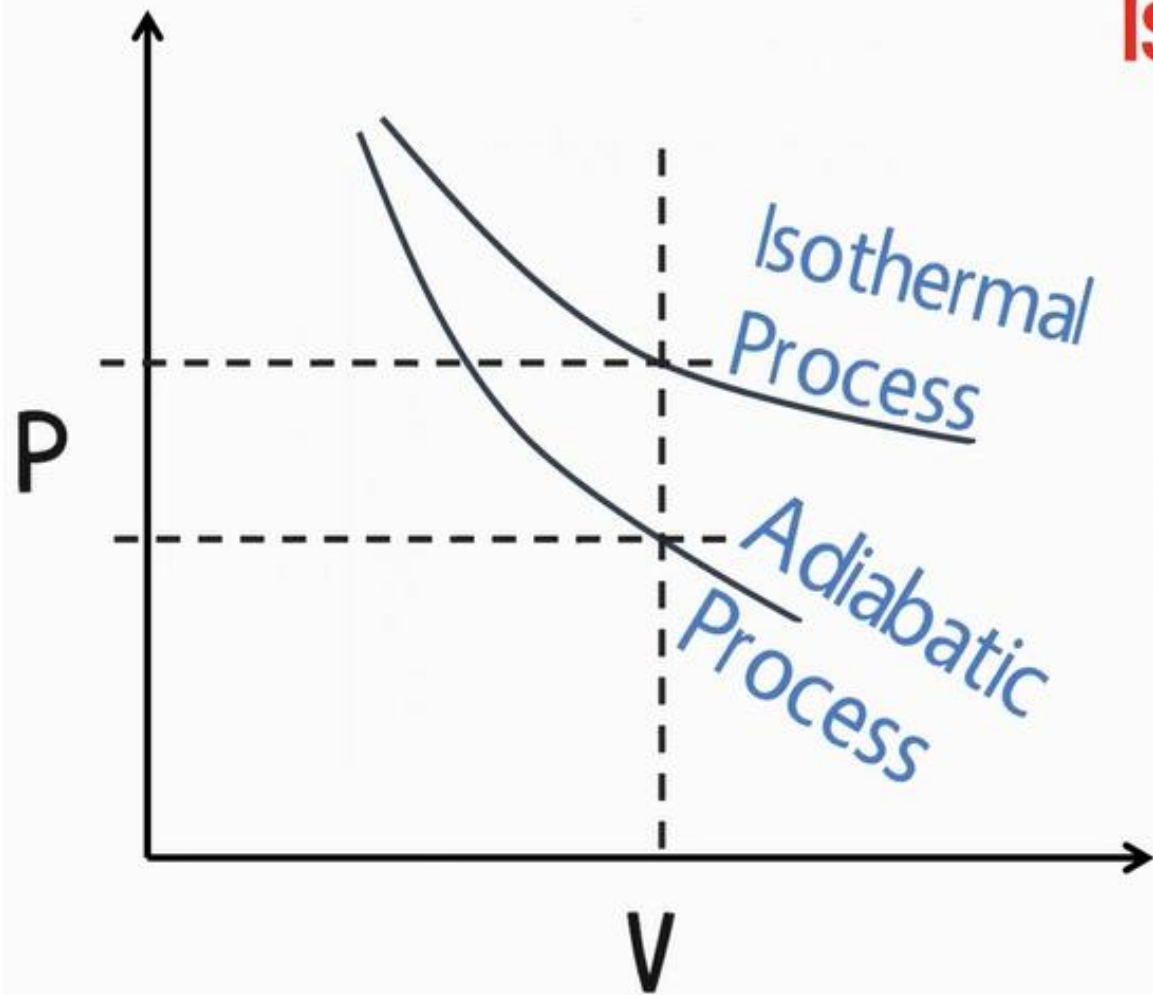
Isothermal Process

$$PV = \text{Constant}$$

$$\uparrow P = \frac{\text{Constant}}{V}$$

Adiabatic Process

$$PV^{\gamma} = \text{Constant}$$

$$\downarrow P = \frac{\text{Constant}}{V^{\gamma}}$$

$$V^{\gamma} > V$$

$$\gamma > 1$$

Zeroth Law of Thermodynamics

Two systems, each separately in thermal equilibrium with a third, are in equilibrium with each other.

A = B = C

FLUID

T=thermometer reading

To=Fluid temperature

Glass Wall

Mercury
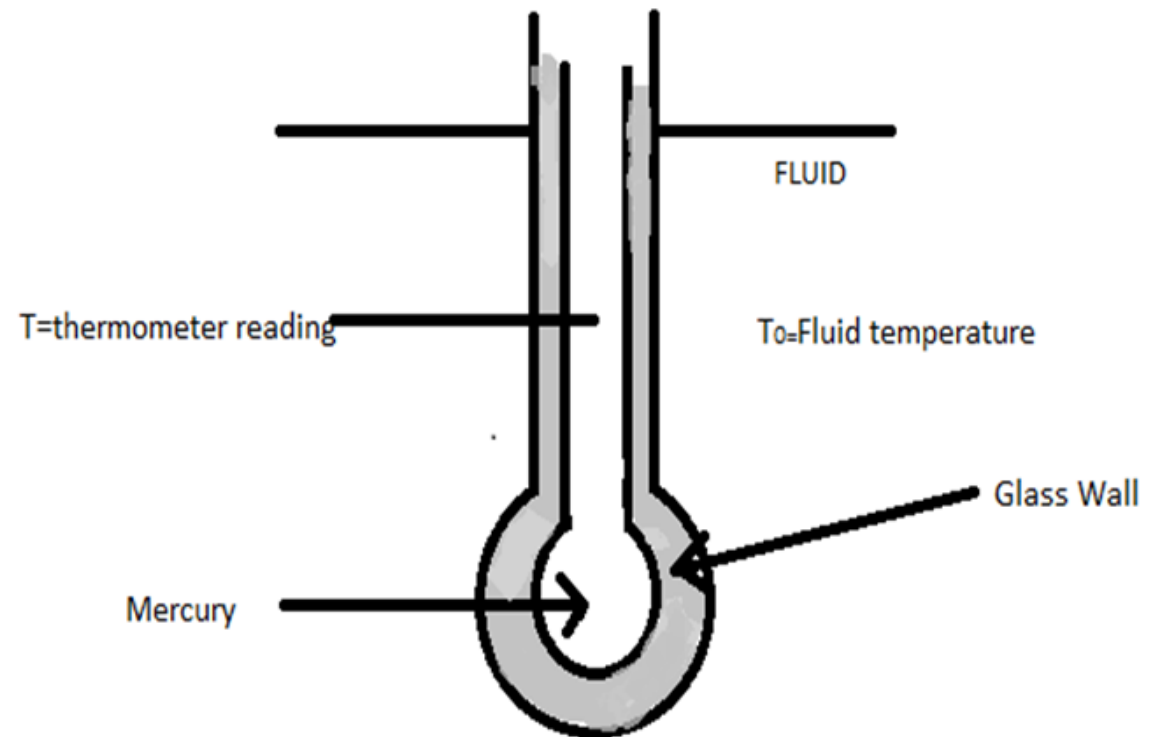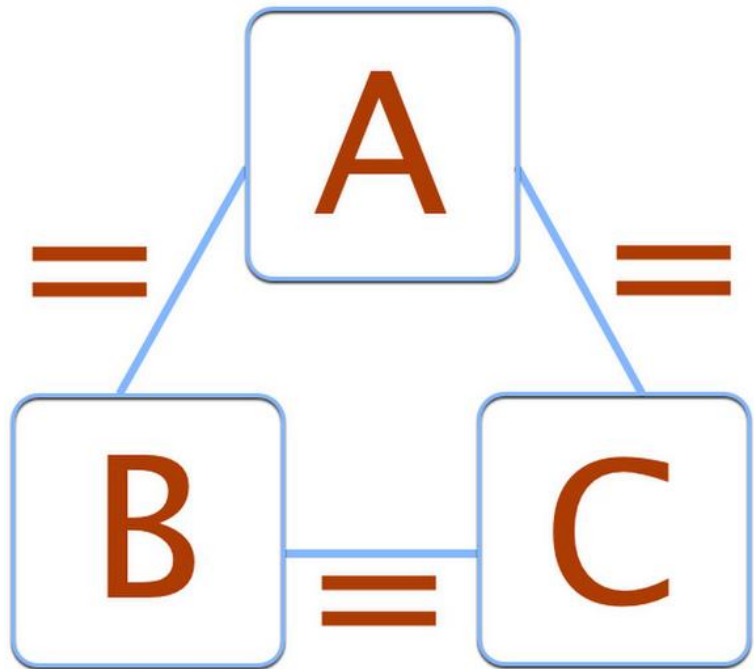
First Law of Thermodynamics

Energy is conserved and heat and work are both forms of energy.

$$\Delta U = \Delta Q + \Delta W$$

ΔQ is the heat supplied to the system

ΔW is the work done on the system

ΔU is the change in internal energy of the system

First Law of Thermodynamics

$$\mathrm{d}U = \mathrm{\bar{d}}Q + \mathrm{\bar{d}}W$$

$$\mathrm{\bar{d}}W = -p\,\mathrm{d}V$$

$\mathrm{d}V$

gas
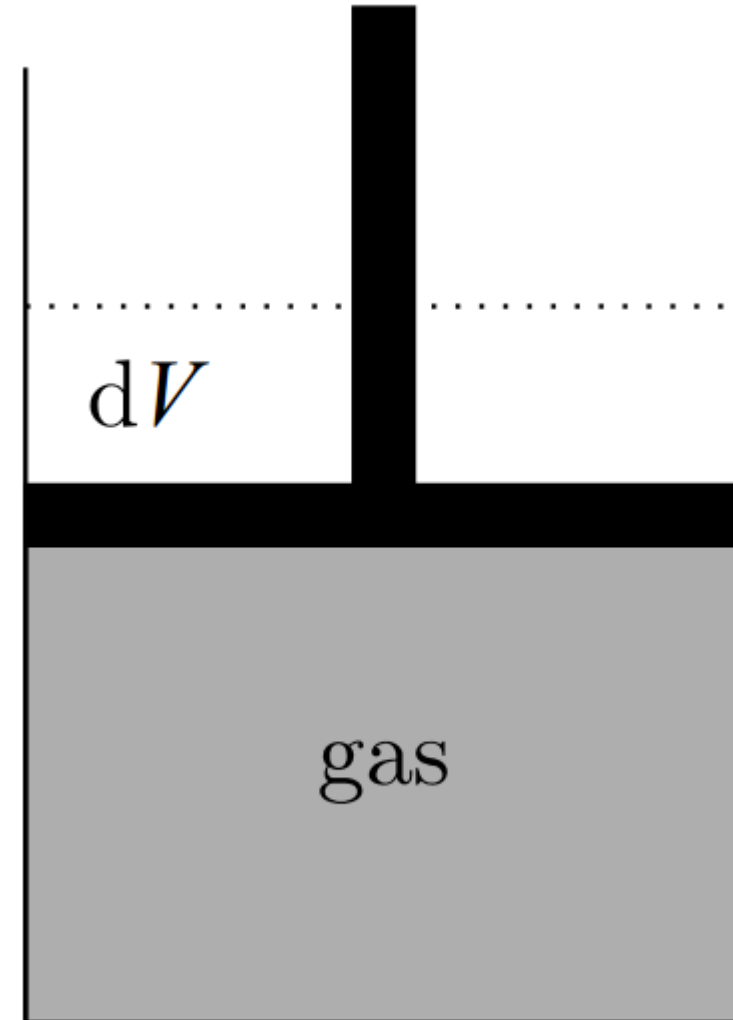
Heat Capacity

In general, the internal energy is a function of temperature and volume, so that we can write $U = U(T,V)$.

Hence a small change in U can be related to changes in T and V by

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

From first law of thermodynamics

$$\text{đ}Q = dU + p\,dV$$

$$\frac{\text{đ}Q}{dT} = \left(\frac{\partial U}{\partial T}\right)_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\frac{dV}{dT}$$

Heat Capacity

$$\frac{\mathrm{d}Q}{\mathrm{d}T} = \left(\frac{\partial U}{\partial T}\right)_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\frac{\mathrm{d}V}{\mathrm{d}T}$$

Heat capacity at constant volume $\quad C_V = \left(\dfrac{\partial Q}{\partial T}\right)_V = \left(\dfrac{\partial U}{\partial T}\right)_V$

Heat capacity at constant pressure

$$C_p = \left(\frac{\partial Q}{\partial T}\right)_p$$

$$= \left(\frac{\partial U}{\partial T}\right)_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\left(\frac{\partial V}{\partial T}\right)_p$$

$$\boxed{C_p - C_V = \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\left(\frac{\partial V}{\partial T}\right)_p}$$

$$\boxed{\mathrm{J\,K^{-1}}}$$

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Heat capacity of an ideal monatomic gas

For an ideal monatomic gas, the internal energy U is due to the kinetic energy and

$$U = \tfrac{3}{2} RT$$

This means that U is only a function of temperature. Hence

$$\left(\frac{\partial U}{\partial V} \right)_T = 0.$$

The equation of state for 1 mole of ideal gas is $pV = RT$.

$$\left(\frac{\partial V}{\partial T} \right)_p = \frac{R}{p}$$

$$C_p - C_V = \left[\left(\frac{\partial U}{\partial V} \right)_T + p \right] \left(\frac{\partial V}{\partial T} \right)_p = R$$

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = \frac{3}{2} R \text{ per mole}$$

$$C_p = C_V + R = \frac{5}{2} R \text{ per mole}$$

The adiabatic index $\qquad \gamma = \dfrac{C_p}{C_V} = \dfrac{5}{3}$

Example 11.3

Is it always true that $dU = C_V \, dT$?

Solution: No, in general eqn 11.10 and eqn 11.15 imply that

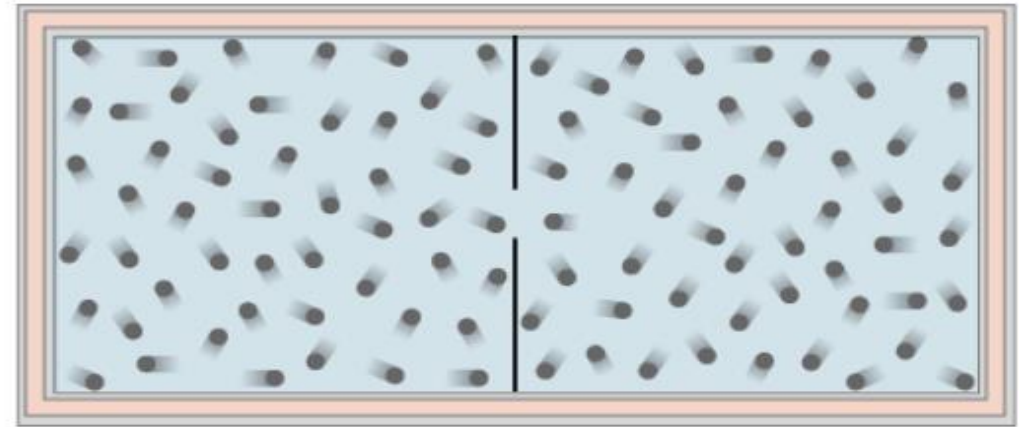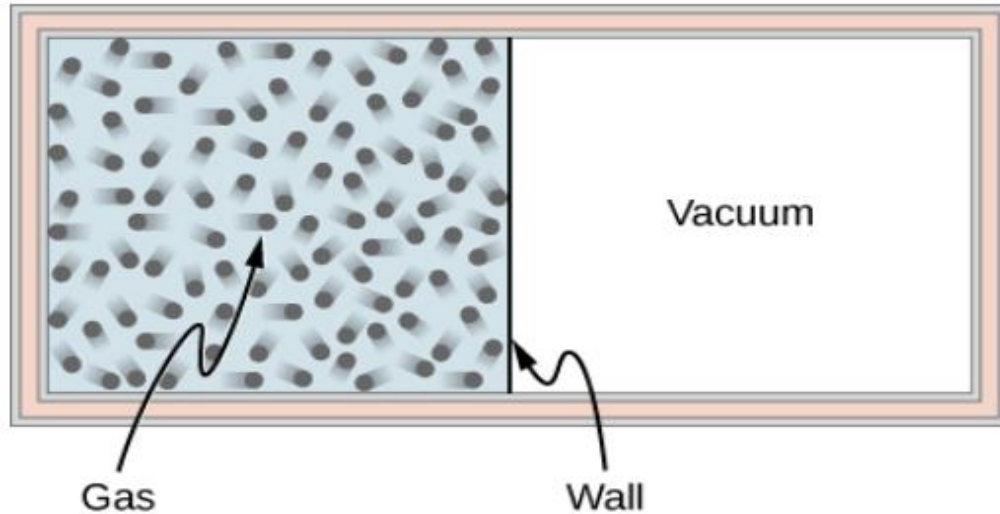$$dU = C_V \, dT + \left(\frac{\partial U}{\partial V}\right)_T dV.$$

For an ideal gas, $\left(\frac{\partial U}{\partial V}\right)_T = 0$ (eqn 11.22) so it is true that

$$dU = C_V \, dT,$$

but for non-ideal gases, $\left(\frac{\partial U}{\partial V}\right)_T \neq 0$ and hence $dU \neq C_v \, dT$.

An ideal gas expanding into vacuum to twice its original volume

Gas   Wall

Vacuum

Gas fills the container

Reversible processes

A **reversible process** is a process in which the system and environment can be restored to exactly the same initial states that they were in before the process occurred, if we go backward along the path of the process. The necessary condition for a reversible process is therefore the quasi-static requirement. Note that it is quite easy to restore a system to its original state; the hard part is to have its environment restored to its original state at the same time. For example, an ideal gas expanding into vacuum to twice its original volume, we can easily push it back with a piston and restore its temperature and pressure by removing some heat from the gas. The problem is that we cannot do it without changing something in its surroundings, such as dumping some heat there.

Irreversible processes

An **irreversible process** is a process in which the system and its environment cannot be restored to their original states at the same time. Because this is what happens in nature, it is also called a natural process. The sign of an irreversible process comes from the finite gradient between the states occurring in the actual process. For example, when heat flows from one object to another, there is a finite temperature difference (gradient) between the two objects. More importantly, at any given moment of the process, the system most likely is not at equilibrium or in a well-defined state. This phenomenon is called **irreversibility**.

The *reversible* process is the ideal process which rarely occurs, while the *irreversible process* is the natural process that is commonly found in nature.

We can make certain processes close to reversible and therefore use the consequences of the corresponding reversible processes as a starting point or reference. In reality, almost all processes are irreversible, and some properties of the environment are altered when the properties of the system are restored. The expansion of an ideal gas, as we have just outlined, is irreversible because the process is not even quasi-static, that is, not in an equilibrium state at any moment of the expansion.

Isothermal expansion of an ideal gas

The word isothermal means 'at constant temperature', and hence in an isothermal process

$$\Delta T = 0.$$

$$dU = C_V \, dT = 0$$

$$\text{d}W = -\text{d}Q \qquad\qquad\qquad \text{d}W = -p \, dV$$

$$\Delta Q = \int \text{d}Q = \int_{V_1}^{V_2} p \, dV = RT \ln \frac{V_2}{V_1}.$$

For an expansion, $V_2 > V_1$, and so $\Delta Q > 0$.

Adiabatic expansion of an ideal gas

The word **adiathermal** means 'without flow of heat'. A system bounded by adiathermal walls is said to be *thermally isolated.* Any work done on such a system produces an adiathermal change. We define a change to be **adiabatic** if it is both adiathermal and reversible. In an adiabatic expansion, therefore, there is no flow of heat and we have

$$\text{đ}Q = 0.$$

The first law of thermodynamics therefore implies that

$$\text{d}U = \text{đ}W.$$

For an ideal gas, $dU = C_V dT$, and using $đW = -p\,dV$ for a reversible change, we find that, for 1 mole of ideal gas,

$$C_V\,dT = -p\,dV = -\frac{RT}{V}\,dV,$$

so that

$$\ln\frac{T_2}{T_1} = -\frac{R}{C_V}\ln\frac{V_2}{V_1}.$$

Now $C_p = C_V + R$, and dividing this by C_V yields $\gamma = C_p/C_V = 1 + R/C_V$, and therefore $-(R/C_V) = 1 - \gamma$, so that

$$TV^{\gamma-1} = \text{constant},$$

or equivalently (using $pV \propto T$ for an ideal gas) $\quad p^{1-\gamma}T^{\gamma} = \text{constant}$

$$\boxed{pV^{\gamma} = \text{constant}}$$

Second Law of Thermodynamics

Clausius' statement of the second law of thermodynamics:
'No process is possible whose sole result is the transfer of heat from a colder to a hotter body.'

Kelvin's statement of the second law of thermodynamics:
'No process is possible whose sole result is the complete conversion of heat into work.'

The Carnot engine

An engine is a system operating a cyclic process that converts heat into work. It has to be cyclic so that it can be continuously operated, producing a steady power.
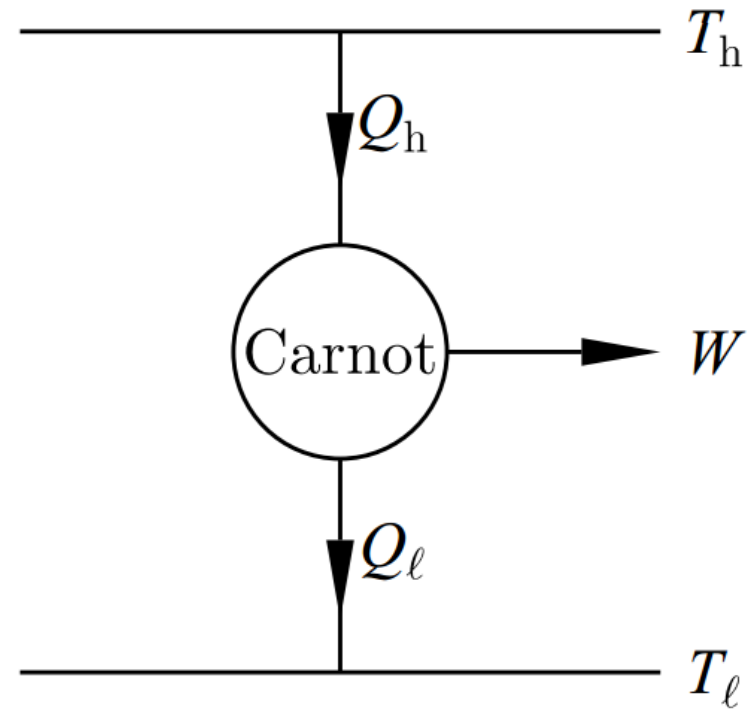
The Carnot engine, which is based upon a process called a Carnot cycle.
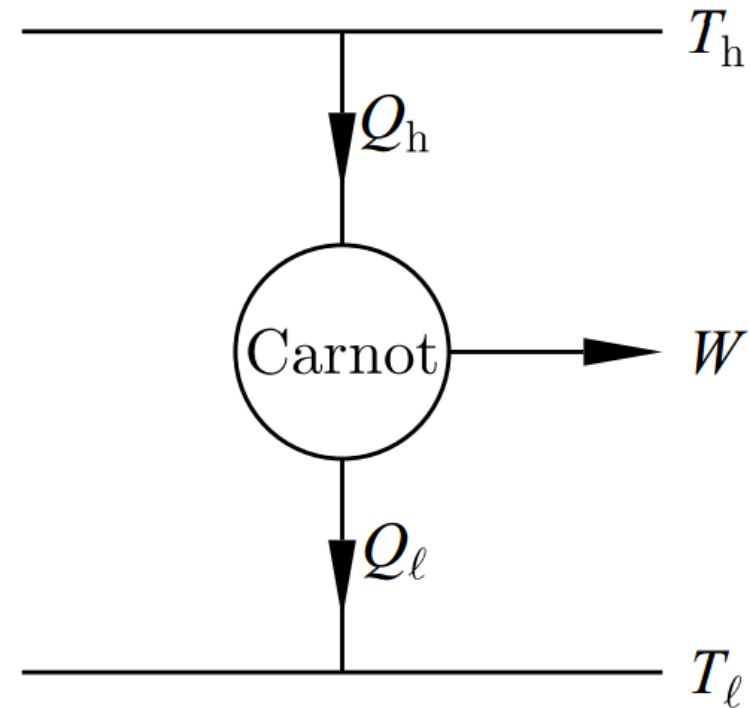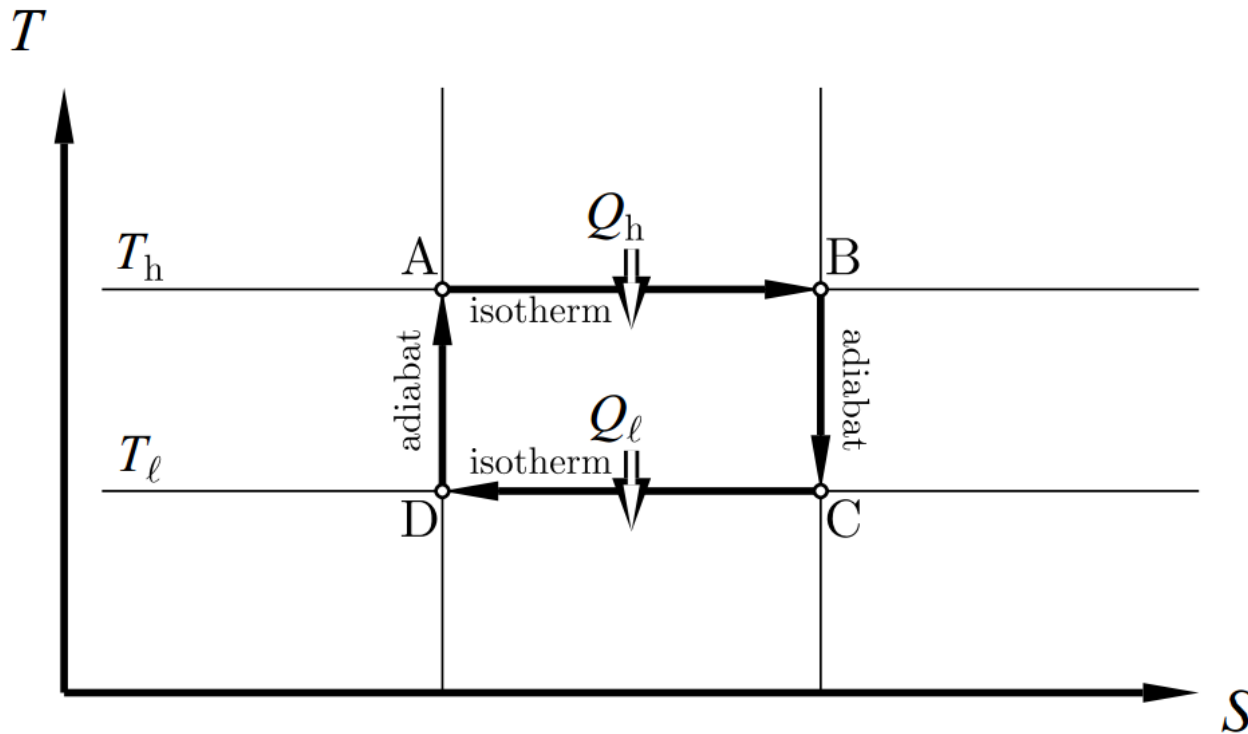
The Carnot engine

$$\eta_{\text{Carnot}} = \frac{Q_h - Q_\ell}{Q_h}$$
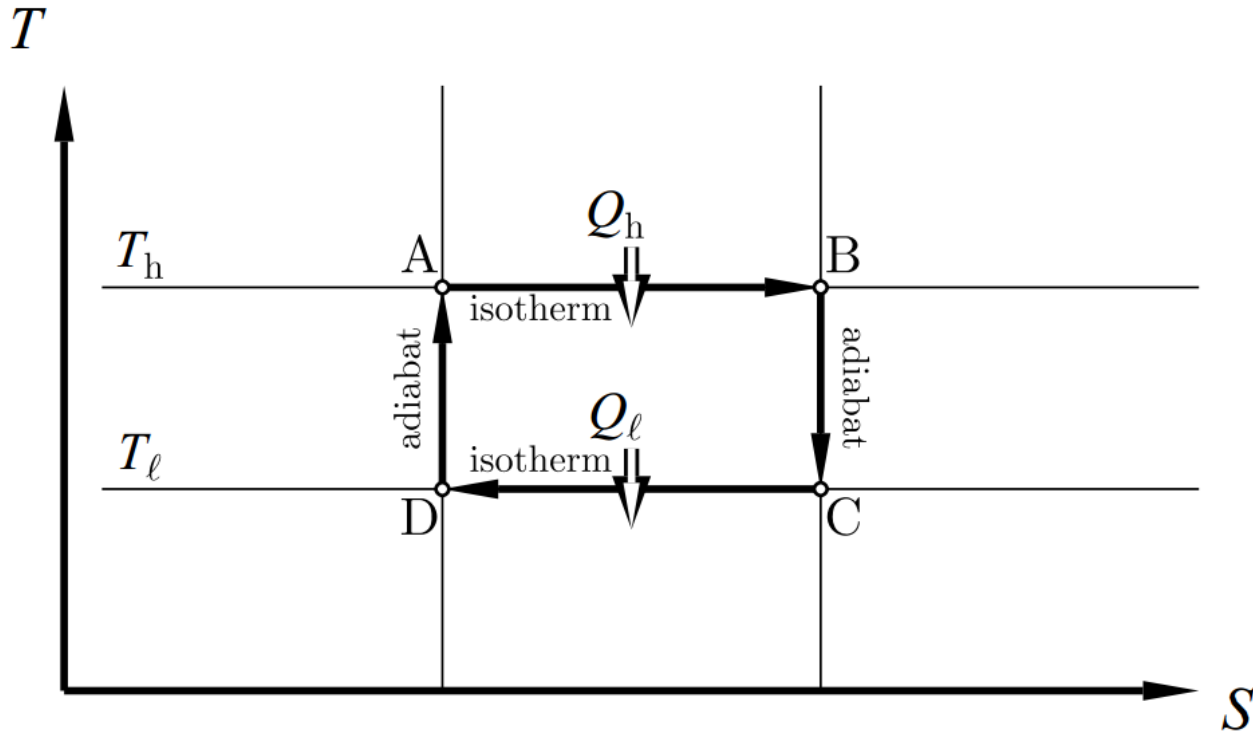
$$\eta_{\text{Carnot}} = \frac{T_h - T_\ell}{T_h}$$

The Carnot engine

$$\eta_{\text{Carnot}} = \frac{Q_{\text{h}} - Q_{\ell}}{Q_{\text{h}}}$$

$$\eta_{\text{Carnot}} = \frac{T_{\text{h}} - T_{\ell}}{T_{\text{h}}}$$

Carnot's theorem:
Of all the heat engines working between two given temperatures, none is more efficient than a Carnot engine.

The Entropy, *S*

Entropy is a thermodynamic quantity representing the unavailability of a system's thermal energy for conversion into mechanical work, often interpreted as the degree of disorder or randomness in the system.

Entropy is the measure of a system's thermal energy per unit temperature that is unavailable for doing useful work. Because work is obtained from ordered molecular motion, the amount of entropy is also a measure of the molecular disorder, or randomness, of a system.

Entropy & Disorder
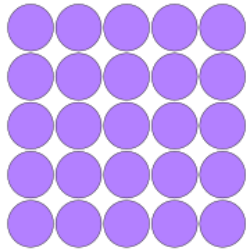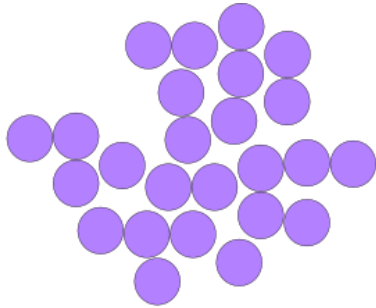
Low Entropy   High Entropy

If you tossed bricks off a truck, which kind of pile of bricks would you more likely produce?

Disorder is more probable than order.

Application to the Universe:
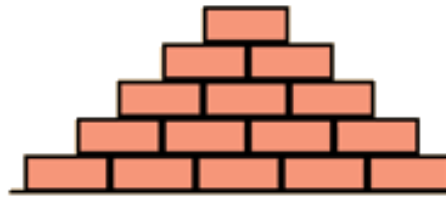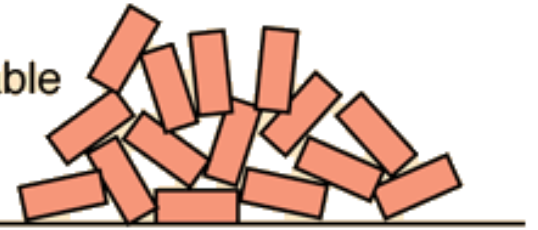Assuming that the Universe can be treated as an isolated system, the first two laws of thermodynamics become:

(1) $U_{\text{Universe}} = \text{constant}$.

(2) S_{Universe} can only increase.

The first law revisited

$$\mathrm{d}U = \mathrm{d}Q + \mathrm{d}W$$

For a reversible change: $\qquad \mathrm{d}Q = T\mathrm{d}S \qquad\qquad \mathrm{d}W = -p\mathrm{d}V$

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V$$

always true

The internal energy is a function of entropy and volume, so that we can write $U = U(S, V)$. Hence a small change in U can be related to changes in S and V by

$$\mathrm{d}U = \left(\frac{\partial U}{\partial S}\right)_V \mathrm{d}S + \left(\frac{\partial U}{\partial V}\right)_S \mathrm{d}V$$

$$T = \left(\frac{\partial U}{\partial S}\right)_V$$

$$p = -\left(\frac{\partial U}{\partial V}\right)_S$$

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Thermodynamics Functions

Internal energy $\qquad U$

Enthalpy $\qquad H = U + pV$

Helmholtz function $\qquad F = U - TS$

Gibbs function $\qquad G = H - TS$

Thermodynamics Functions

Function of state		Differential	Natural variables	First derivatives	
Internal energy	U	$dU = TdS - pdV$	$U = U(S,V)$	$T = \left(\frac{\partial U}{\partial S}\right)_V,$	$p = -\left(\frac{\partial U}{\partial V}\right)_S$
Enthalpy	$H = U + pV$	$dH = TdS + Vdp$	$H = H(S,p)$	$T = \left(\frac{\partial H}{\partial S}\right)_p,$	$V = \left(\frac{\partial H}{\partial p}\right)_S$
Helmholtz function	$F = U - TS$	$dF = -SdT - pdV$	$F = F(T,V)$	$S = -\left(\frac{\partial F}{\partial T}\right)_V,$	$p = -\left(\frac{\partial F}{\partial V}\right)_T$
Gibbs function	$G = H - TS$	$dG = -SdT + Vdp$	$G = G(T,p)$	$S = -\left(\frac{\partial G}{\partial T}\right)_p,$	$V = \left(\frac{\partial G}{\partial p}\right)_T$

Maxwell's relation

If a state function *f* is a function of variables *x* and *y* then a change in *f* can be written as

$$\mathrm{d}f = \left(\frac{\partial f}{\partial x}\right)_y \mathrm{d}x + \left(\frac{\partial f}{\partial y}\right)_x \mathrm{d}y.$$

Because d*f* is an exact differential, we have

$$\left(\frac{\partial^2 f}{\partial x \partial y}\right) = \left(\frac{\partial^2 f}{\partial y \partial x}\right).$$

Hence writing

$$F_x = \left(\frac{\partial f}{\partial x}\right)_y \quad \text{and} \quad F_y = \left(\frac{\partial f}{\partial y}\right)_x,$$

we have that

$$\left(\frac{\partial F_y}{\partial x}\right) = \left(\frac{\partial F_x}{\partial y}\right).$$

The Maxwell relation based on *G* can be derived as follows. We write down an expression for d*G*:

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p.$$

We can also write

$$\mathrm{d}G = \left(\frac{\partial G}{\partial T}\right)_p \mathrm{d}T + \left(\frac{\partial G}{\partial p}\right)_T \mathrm{d}p,$$

and hence we can write $S = -\left(\frac{\partial G}{\partial T}\right)_p$ and $V = \left(\frac{\partial G}{\partial p}\right)_T$.

Because dG is an exact differential, we have that

$$\left(\frac{\partial^2 G}{\partial T \partial P}\right) = \left(\frac{\partial^2 G}{\partial p \partial T}\right),$$

and hence we have the following Maxwell relation:

$$-\left(\frac{\partial S}{\partial p}\right)_T = \left(\frac{\partial V}{\partial T}\right)_p$$

Maxwell's relations:

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$$

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$$

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p.$$

Third Law of Thermodynamics

Nernst's statement of the third law
Near absolute zero, all reactions in a system in internal equilibrium take place with no change in entropy.

Planck's statement of the third law
The entropy of all systems in internal equilibrium is the same at absolute zero, and may be taken to be zero.

Simon's statement of the third law
The contribution to the entropy of a system by each aspect of the system which is in internal thermodynamic equilibrium tends to zero as $T \rightarrow 0$.

The Clausius–Clapeyron Equation

$$\frac{dP_0}{dT} = \frac{\Delta S}{\Delta V}$$

$$\frac{dP_0}{dT} = \frac{Q_L}{T\,\Delta V}$$

The latent heat Q_L is the quantity of heat which is required to convert the substance from phase 1 to phase 2:

$$Q_L = T\,\Delta S \ .$$

The ratio of the specific volume of water to that of ice is 1.000:1.091 at 0°C and 1 atm. The heat of melting is 80 cal/g. Calculate the slope of the melting curve.

The volume change upon melting if ice is $V_L - V_S = (1.00 - 1.091)\,\text{cm}^3/\text{g} = -0.091\,\text{cm}^3\text{g}^{-1}$. The latent heat of melting per g is $Q = 80\,\text{cal}/\text{g} = 80 \times 42.7\,\text{atm}\,\text{cm}^3/\text{g}$. From this, it follows that the slope of the melting curve of ice near 0°C is

$$\frac{dP}{dT} = -\frac{80 \times 42.7}{273 \times 0.091}\,\frac{\text{atm}}{\text{K}} = -138\,\text{atm}/\text{K}\,.$$