

Course Syllabus and Plan

Principles of thermodynamics (with applications to simple fluids); thermodynamic potentials: enthalpy, Helmholtz potential, Gibbs potential; Entropy; conditions of equilibrium, concepts of stable, metastable and unstable equilibrium.

Reading:

- ♣ Concepts in Thermal Physics by Stephen J. Blundell and Katherine M. Blundell
- ♣ Fundamentals of Statistical and Thermal Physics by F. Reif
- ♣ Heat and Thermodynamics by M. W. Zemansky and R. H. Dittman

Disclaimer: This is not a text book. Rather, these lecture notes are written by **Dr. Ritwik Mondal**, and edited by Dr. Tusharkanti Dey, Department of Physics, IIT (ISM) Dhanbad. The contents are taken from several text books. Please read the above books for your reference. If you find any mistakes or typos, please report to Dr. Tusharkanti Dey.

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Principles of Thermodynamics

The first question is what is Temperature?

Temperature is something that we measure using a thermometer.

But this is an operational definition because it tells you how to measure the quantity in question.

Let us understand how the thermometer works. If you want to measure the temperature of your body, you must stick the thermometer to your body, wait for a while, and then you look at the reading on the thermometer scale. Eventually, the mercury inside the thermometer expands or contracts as the temperature of your body goes up or down. The volume taken by mercury tells you the temperature.

This means the thermometer relies on the fundamental fact that when you put two objects in contact with each other for a sufficiently long time, they tend to have the same temperature.

Temperature is a thing that is the same for two objects if they are kept in contact for long enough.

We might call this as a theoretical description, but this is rather vague. What kind of contact are we talking about and what is meant by long enough?

When two objects are kept in contact for long enough, they are in thermal equilibrium.

The time required for a system to come to thermal equilibrium is called relaxation time.

The contact needs a physical contact where the two objects can exchange energy in terms of heat. So, the thermal equilibrium requires exchange of heat energy. Similarly, there are other other equilibrium such as diffusive equilibrium and mechanical equilibrium where the particles and volumes are exchanged, respectively.

So, now we have some idea about Temperature that is measured in Kelvin and Celsius. The room temperature is 300 K (30 °C) and absolute zero 0 K that is -273°C. The relation between Kelvin and Celsius is

$$T \text{ in K} = T \text{ in } ^\circ\text{C} + 273 \quad (1)$$

Zeroth Law of thermodynamics: Two systems in thermal contact eventually arrive at a state of thermal equilibrium. This state is uniquely defined by temperature, which is a universal function of the state properties and the internal energy.

If a system A is in equilibrium with system B, and if system B is in equilibrium with system C, then system A is in equilibrium with system C. This is called the zeroth law of thermodynamics and implies the construction of a universal temperature scale (stated first by Joseph Black in the 18th century, and named much later by Guggenheim).

If a system is in thermal equilibrium, it is assumed that the energy is distributed uniquely over the volume. Once the energy of the system increases, the temperature of the system also increases.

Heat and Work

Thermodynamics mostly deals with three related concepts: temperature, heat and energy. We have understood about temperature such that if a system releases energy, the temperature goes down and in contrary if the system consumes energy, the temperature goes up.

From the energy conservation laws, if the energy of a system increases, that additional energy must have come from outside. The mechanisms through which the energy comes into a system or goes out of a system can be classified under two categories: heat and work.

Heat is defined as spontaneous flow of energy from one object to the other, caused by the temperature difference between the objects. For example heat flows from warm radiator to a cold room. Transfer of heat is a spontaneous process.

Work on the other hand is not a spontaneous process. A work is done when you stir a cup of coffee, push on a piston. While a work is done on a system the energy increases and the temperature tends to rise. We often focus on the effects the system has on its surroundings.

Notice that the heat and work defines energy in transit meaning those come into or go out of a system. Therefore, we refer to total internal energy of the system and denote by U . The heat and work are defined as Q and W , respectively. The sum $Q + W$ is the total energy that enters to the system. Let's say the initial energy of a system was U_0 and now it has energy U . Thus, the change in total internal energy is

$$U - U_0 = dU = dQ + dW \quad (2)$$

This is true by virtue of the conservation of energy. This is known as **First Law of**

Thermodynamics.

The sign of work done can be positive or negative depending on the reference. If the reference is internal energy U , something that increases the internal energy is accounted as positive. If work is done on the system, the internal energy increases, and thus the work done on the system is **Positive**, while the work done by the system is **Negative**. Therefore, the first law of thermodynamics is

$$dU = dQ + dW \quad (3)$$

On the other hand, if the reference point is an engine, we provide energy to the engine so that it works. If I heat up the system that would lead to the change in internal energy plus the work done. Thus, the first law can be written as

$$dQ = dU + dW \Rightarrow dU = dQ - dW \quad (4)$$

However, the latter convention is a bit confusing! We will focus on the first definition though. Remember that both definitions should converge to the same result.

Exact differentials:

Notice that we have introduced two notions for change in internal energy and the heat, work done.

An expression $F_1(x, y)dx + F_2(x, y)dy$ can be called as an exact differential if we can write

$$df = \left(\frac{\partial f}{\partial x} \right)_y dx + \left(\frac{\partial f}{\partial y} \right)_x dy \quad (5)$$

where

$$F_1(x, y) = \left(\frac{\partial f}{\partial x} \right)_y ; \quad F_2(x, y) = \left(\frac{\partial f}{\partial y} \right)_x \quad (6)$$

In vector form one can write $\mathbf{F} = \nabla f$ and the integral is

$$\int_1^2 F_1(x, y)dx + F_2(x, y)dy = \int_1^2 \nabla f \cdot d\mathbf{r} = \int_1^2 df = f(2) - f(1) \quad (7)$$

The integral over the exact differential do not depend on the paths. This is the essence of an exact differential.

For inexact differential, the information of initial and final points are not sufficient. Therefore, those are path dependent.

The exact differentials are usually written as df while the inexact differentials are $\bar{d}f$.

Internal energy is an exact differential while the heat and work done are inexact differentials.

Ideal Gas Law:

The ideal gas law is

$$PV = nRT \quad (8)$$

n is the number of moles and R is the universal constant that is expressed in

$$R = 8.31 \frac{\text{J}}{\text{mol.K}} \quad (9)$$

Considering the Avogadro's number $N_A = 6.022 \times 10^{23}$, the number of molecules can be calculated using

$$N = n \times N_A \quad (10)$$

We then plug these two in the ideal gas law equation to find out

$$PV = nRT \Rightarrow PV = N \times \left(\frac{R}{N_A} \right) \times T = NkT \quad (11)$$

k is the Boltzmann constant measured as $k = 1.38 \times 10^{-23} \text{ J/K}$.

Internal Energy:

Total internal energy is a measure of thermal energy that we will be speaking of. Remember, there can be other types of energy (e.g., static energy, rest mass energy). However, we will be restricting ourselves only with the thermal energy in this course. Equipartition theorem says that at any given temperature T , the average energy of any degree of freedom is $\frac{1}{2}kT$.

If a system of molecules has N no. of molecules, each with degrees of freedom f , the total internal energy can be calculated as

$$U = N \cdot f \cdot \frac{1}{2}kT \quad (12)$$

One can imagine that if the temperature of the system is not changed, then there is no change in energy.

Application to an Ideal Gas

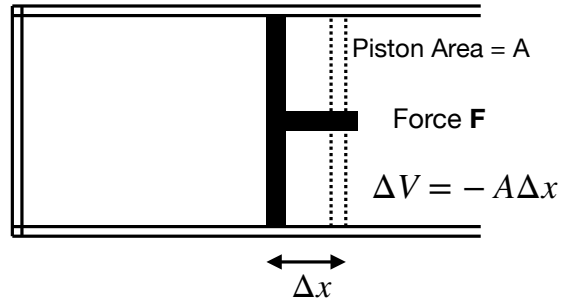


Figure 1: When the piston moves inward, the volume of the gas changes by ΔV (a negative amount) and the work done on the gas (assuming quasistatic compression) is $-P\Delta V$

Work done on a system of an ideal gas is achieved by compressing by a piston. The work done is calculated as

$$W = \mathbf{F} \cdot d\mathbf{r} \quad (13)$$

For an ideal gas, it is more convenient to express force in terms of pressure P and

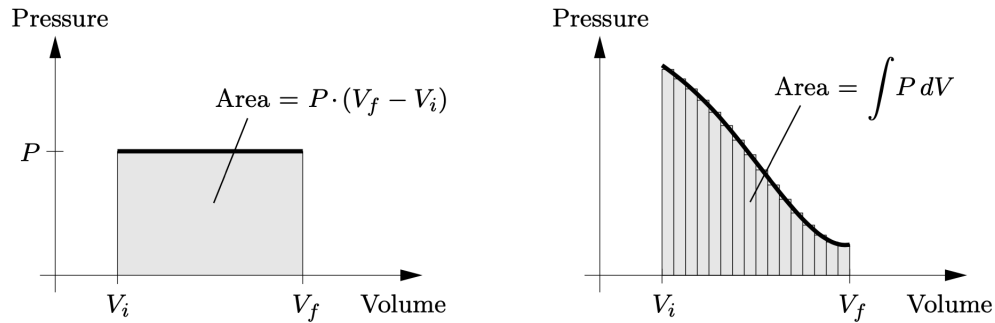


Figure 2: The work done is calculated using the difference between volumes for constant pressure. However, if the pressure is not constant, the curve could be broken to many infinitesimal area and the work done is calculated using the sum over all the area under the infinitesimal curve.

volume $\Delta V = A\Delta x$. When the force is parallel to the displacement, we have the

work done as

$$\begin{aligned} dW &= F\Delta x = PA\Delta x \\ &= -P\Delta V = -PdV \end{aligned} \quad (14)$$

For a continuous process, one could write down

$$W = - \int_{V_i}^{V_f} P(V) dV \quad (15)$$

We have to note down that such change of gas volume is quasi-static meaning the volume change is slow enough such that the pressure remains constant inside. Remember that no process is quasi-static in practice, however, this is a very good approximation. If the pressure is constant then it is easy to calculate the work. However, if the pressure is not constant, then we break the area under $P - V$ curve to infinitesimal volumes such that the pressure in each area remains constant. To get a total work done, we can add all the contributions.

We will learn about two extreme processes while compressing a gas. Isothermal compression is very slow such that the temperature of the gas is not changed. Adiabatic compression is very fast where no heat transfer happens during such process.

Reversible Process: A reversible process is one in which both the system and its environment can return to exactly the states they were in by following the reverse path.

Expansion or compression of a string, melting of ice.

Irreversible Process: An irreversible process is one in which the system and its environment can not return together to exactly the states that they were in.

Burning of fuel.

Quasi-static Process: When a process in which the system remains close to an equilibrium state at each time, such process will be termed a quasi-static process or quasi-equilibrium process. For example, if a person is coming down from the roof to the ground floor with the help of ladder steps then it is a quasi-static process. But if he jumps from the roof to the ground floor then it will not be a quasi-static process.

All the reversible processes are quasi-static but not all the quasi-static processes are reversible.

Cyclic Process: During a process, if the initial and final thermodynamic variables are exactly the same, then the process is called a cyclic process. The total change in internal energy is zero in this case, however, the work done on the system and the heat are not zero, but the amount is exactly same and opposite.

Isothermal Process: The temperature remains constant during the isothermal process meaning the change in internal energy is zero.

Isobaric Process: The pressure remains constant during this process.

Isochoric Process: The volume remains constant during this process. Therefore, the work done on the system or by the system is zero. ($dW = -PdV = 0$)

Adiabatic Process: During this process the change of heat is zero. Such a process can occur when it is perfectly insulated from the surroundings. While this is not possible in reality, one can approximate a process as an adiabatic process that happens very rapidly so that the system does not get time for heat exchange with the surroundings.

Isothermal Compression:

For isothermal process, we can calculate the work done as

$$W = -NkT \int_{V_i}^{V_f} \frac{dV}{V} = -NkT (\ln V_f - \ln V_i) = NkT \ln \left(\frac{V_i}{V_f} \right) \quad (16)$$

The work done is positive if $V_i > V_f$ that means the gas is compressed - work done

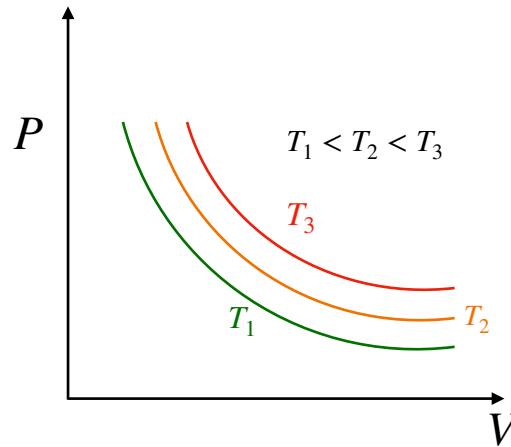


Figure 3: Isothermal Process

on the gas. On the other hand, work done is negative if $V_i < V_f$ means gas expands - work done by the gas.

We have talked about isothermal process where the temperature remains constant. In this process, heat must flow out into the environment. We can use first law of thermodynamics to calculate the heat flow. As the temperature remains constant, the change in internal energy is zero. From the first law of thermodynamics:

$$dU = dQ + dW \Rightarrow dQ = -dW = -NkT \ln \left(\frac{V_i}{V_f} \right) = NkT \ln \left(\frac{V_f}{V_i} \right) \quad (17)$$

Note that one can write down the exact differential as

$$dV = \left(\frac{\partial V}{\partial P} \right)_T dP + \left(\frac{\partial V}{\partial T} \right)_P dT \quad (18)$$

For isothermal compression, we obtain

$$dV = \left(\frac{\partial V}{\partial P} \right)_T dP \quad (19)$$

The work done during this process can be generally written as

$$W = - \int_{P_i}^{P_f} P \left(\frac{\partial V}{\partial P} \right)_T dP = \int_{P_i}^{P_f} \kappa P V dP \quad (20)$$

where the isothermal compressibility is expressed as

$$\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \quad (21)$$

Adiabatic Compression:

The adiabatic compression is such that no heat flows out of the system or into the system. However, in this process, the total energy of the system will increase as we learn.

$$dU = dQ + dW = dW \quad (22)$$

We use the equipartition theorem and the infinitesimal change in internal energy is expressed as

$$dU = \frac{F}{2} Nk dT = dW = -PdV \quad (23)$$

(Degree of freedom is taken as F to avoid any confusion with the subscript in V_f and T_f)

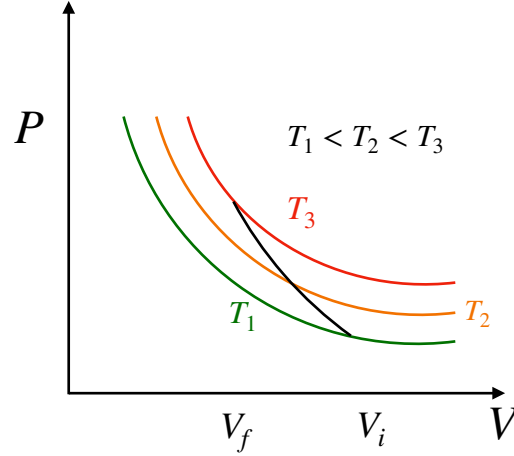


Figure 4: The black curve denotes adiabatic process

$$\begin{aligned}
 &\Rightarrow \frac{F}{2} Nk dT = -PdV \\
 &\Rightarrow \frac{F}{2} Nk dT = -\frac{NkT}{V} dV \\
 &\Rightarrow \frac{F}{2} \frac{dT}{T} = -\frac{dV}{V} \\
 &\Rightarrow \frac{F}{2} \ln \left(\frac{T_f}{T_i} \right) = -\ln \left(\frac{V_f}{V_i} \right) \\
 &\Rightarrow V_f T_f^{F/2} = V_i T_i^{F/2}
 \end{aligned} \tag{24}$$

Therefore, the equation for adiabatic compression is $VT^{F/2} = \text{Constant}$.

One could also employ the ideal gas law to replace T with P and the equation takes a new form

$$V^\gamma P = \text{Constant} \tag{25}$$

where $\gamma = \frac{F+2}{F} = \frac{C_P}{C_V}$ is called adiabatic constant.

Heat Capacity: The heat capacity of an object is the amount of heat needed to raise its temperature by one degree. This means

$$C = \frac{\Delta Q}{\Delta T} \tag{26}$$

You can imagine that a large amount of heat is needed if the system is large enough. Therefore, one often talks about the specific heat capacity of a system meaning per unit mass.

From equation 4 we obtain

$$\delta Q = dU + PdV \quad (27)$$

We know that the state of a gas can be described in terms of only two coordinates out of P, V, and T as independent variables. Since U is a state function, we can express U as a function of T and V, i.e. $U=U(T, V)$, and the differential of U can be written as

$$dU = \left(\frac{\partial U}{\partial T} \right)_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV \quad (28)$$

Substituting this in equation 27, we get,

$$\delta Q = \left(\frac{\partial U}{\partial T} \right)_V dT + \left\{ \left(\frac{\partial U}{\partial V} \right)_T + P \right\} dV \quad (29)$$

Now, at constant volume when the work done is 0, the Heat Capacity at Constant Volume, denoted as

$$C_V = \left(\frac{\partial Q}{\partial T} \right)_V = \left(\frac{\partial U}{\partial T} \right)_V \quad (30)$$

In everyday life, the systems often expand as their temperature is increased. Therefore, a more general way to calculate the Heat Capacity at constant pressure

$$C_P = \left(\frac{\partial Q}{\partial T} \right)_P = \left(\frac{\partial U}{\partial T} \right)_V \left(\frac{\partial T}{\partial T} \right)_P + \left\{ \left(\frac{\partial U}{\partial V} \right)_T + P \right\} \left(\frac{\partial V}{\partial T} \right)_P \quad (31)$$

$$C_P = \left(\frac{\partial U}{\partial T} \right)_V + \left\{ \left(\frac{\partial U}{\partial V} \right)_T + P \right\} \left(\frac{\partial V}{\partial T} \right)_P \quad (32)$$

$$C_P = C_V + \left\{ \left(\frac{\partial U}{\partial V} \right)_T + P \right\} \left(\frac{\partial V}{\partial T} \right)_P \quad (33)$$

$$C_P - C_V = \left\{ \left(\frac{\partial U}{\partial V} \right)_T + P \right\} \left(\frac{\partial V}{\partial T} \right)_P \quad (34)$$

Considering ideal gas equation (internal energy is kinetic and intermolecular attraction is 0),

$$P \left(\frac{\partial V}{\partial T} \right)_P = R \quad (35)$$

$$\left(\frac{\partial U}{\partial V} \right)_T = 0 \quad (36)$$

Hence we get,

$$C_P - C_V = R \quad (37)$$

This is called Mayer's formula.

Second Law of Thermodynamics

We have understood about first law of thermodynamics. A process that is not in agreement with the first law, will not occur. However, what about the converse? That is, is agreement with the first law, enough for us to conclude that a process can occur?

It is common experience that there are processes that occur in only one direction, and not the other. Since all three of dU , dQ , and dW change sign when you reverse a process, if a forward process obeys the first law of thermodynamics, then so does the reversed version! Yet, as is our common experience, heat flows readily from a hot body to a cold body - but it stubbornly refuses to go the other way. Of course, if 10 J of heat left the cold body and the same amount entered the hotter one, the 1st law will be perfectly satisfied - so whatever prevents this from happening has to be a different law of nature. This law, which we will soon elaborate, is the second law of thermodynamics.

The first law of thermodynamics rules out perpetual motion machines of the first kind - imaginary contraptions that produce work without any energy input, or at least produce more work than the energy that is put in. Now that a lot of experimental data has convinced us of the futility of the quest for such machines, we may try to get a machine to run forever in a more subtle fashion. Imagine a boat, which can extract heat from the surrounding water and convert it completely into work by means of some cyclic process. Of course, since you are not asking for more work to be produced than the heat energy put in, there is no violation of the first law here. Now, this work that the boat's engine produces turns the propellers and causes it to move through water. If this had been an one-off thing, the boat would have come to a halt a bit later, all its energy dissipated by friction with the water. Where does the energy go? Its back in the water in the form of heat. However, this means that the water is back to the state was in before the boat took in the heat and so we are in a position to repeat the whole thing again, and again and again ... ! What I have described just now is called a perpetual motion machine of the second kind - a machine that keeps on going, once started, without ever needing re-fueling. Life would have been wonderful if we could build such an engine - no need to spend precious foreign exchange on the oil reserve! This sort of machine is not in conflict with the first law in any way. Energy conservation alone does not forbid us from building them. Unfortunately, the machines themselves stubbornly refuse

to be built as hundreds and thousands of experiments have shown over and over again! So convinced are we of the nonexistence of the perpetual motion machine of the second kind, that we have made this into a law. The law is - you guessed it - the second law of thermodynamics.

Before we dive deeper into this, just ponder over one point. All of you know that today we are right in the middle of a deep energy crisis. However, as you have read over and over again, energy is something that cannot be created or destroyed and can only be converted from one form to another. How can there be a crisis of depletion in something that is, by its very nature, indestructible? Think about it a bit and you will realize that it is not enough to have energy, the form in which the energy is available is very important! One reason that electricity drives modern civilization is that electrical energy can be easily converted to the form you may need for any given job. Once the energy is used up, it usually lands up in the form of heat in the long run - and it is here that we face the crunch. Once energy becomes heat, there is no way that it can be reconverted to some other useful form of energy completely. So, what becomes heat remains, to a large extent, useless energy! What prevents us from converting heat completely into work, thereby beating the energy crisis, is none other than the second law of thermodynamics.

Clausius Statement: No cyclic process is possible where heat transfers from colder object to a hotter object.

The second law of thermodynamics states about the conversion of energies. One can easily convert work into heat, however, the conversion of all the heat into work is impossible. This is exactly the statement made by Kelvin.

Kelvin statement: No cyclic process is possible where all the heat is converted into work.

Engine: Engines are the devices that convert heat into work. According to the second law of thermodynamics, all the heat cannot be converted to work. Thus, the efficiency of the engine is defined as

$$\eta = \frac{\text{Amount of work done}}{\text{Amount of Heat absorbed}} = \frac{W}{Q_+} \quad (38)$$

Of course we see from energy conservation that

$$Q_+ = W + Q_- \quad (39)$$

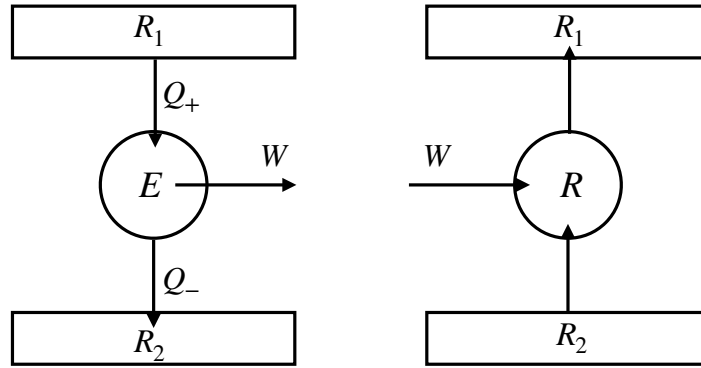


Figure 5: A heat engine absorbs heat energy from a hot reservoir and a work is done. A refrigerator can be thought of reverse of an engine.

The efficiency is then:

$$\eta = \frac{Q_+ - Q_-}{Q_h} = 1 - \frac{Q_-}{Q_+} \quad (40)$$

Therefore the efficiency of a heat engine cannot be greater than 1.

Carnot's Engine:

The Carnot's engine consists of Isothermal Expansion, Adiabatic Expansion, Isothermal Compression and Adiabatic Compression.

Step I: Isothermal expansion The change of internal energy is zero $dU_1 = 0$ and thus

$$dQ_1 = -dW_1 = NkT_1 \ln \left(\frac{V_2}{V_1} \right) \quad (41)$$

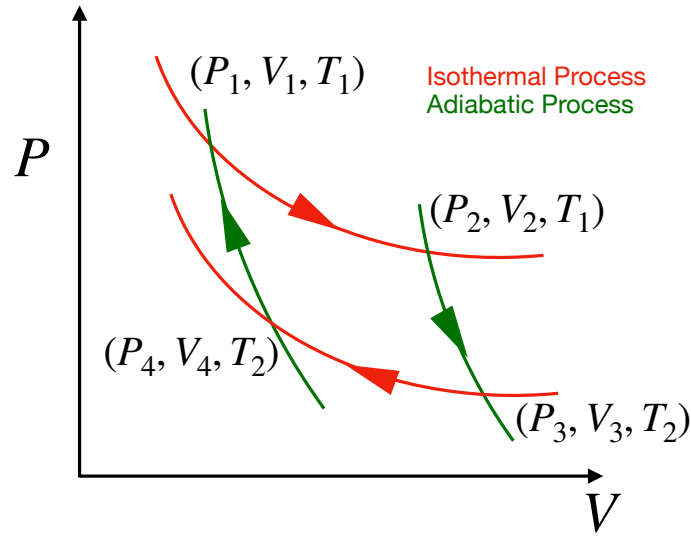


Figure 6: The cyclic processes of a Carnot's Engine

Step II: Adiabatic expansion The change of heat energy is zero $dQ_2 = 0$ and thus

$$dW_2 = dU_2 = \frac{3}{2}Nk(T_2 - T_1) \quad (42)$$

Also, we have

$$T_1^{3/2}V_2 = T_2^{3/2}V_3 \Rightarrow \left(\frac{T_1}{T_2} \right)^{3/2} = \frac{V_3}{V_2} \quad (43)$$

Step III: Isothermal Compression The change of internal energy is zero $\Delta U_3 = 0$ and thus

$$dQ_3 = -dW_3 = NkT_2 \ln \left(\frac{V_4}{V_3} \right) \quad (44)$$

Step IV: Adiabatic compression The change of heat energy is zero $dQ_4 = 0$ and thus

$$dW_4 = dU_4 = \frac{3}{2}Nk(T_1 - T_2) \quad (45)$$

Also, we have

$$T_2^{3/2}V_4 = T_1^{3/2}V_1 \Rightarrow \left(\frac{T_1}{T_2}\right)^{3/2} = \frac{V_4}{V_1} \quad (46)$$

Equating Eq (35) and (38) we get

$$\frac{V_3}{V_2} = \frac{V_4}{V_1} \Rightarrow \frac{V_4}{V_3} = \frac{V_1}{V_2} \quad (47)$$

One could easily see that the total change in internal energy is zero. Now we also conclude the following:

$$\frac{dQ_3}{T_2} = Nk \ln \left(\frac{V_4}{V_3} \right) = Nk \ln \left(\frac{V_1}{V_2} \right) = -\frac{dQ_1}{T_1} \Rightarrow \frac{dQ_1}{T_1} + \frac{dQ_3}{T_2} = 0 \quad (48)$$

For a cyclic process there has to be some state function that does not change. Therefore for a reversible cyclic process we have

$$\oint \frac{dQ}{T} = 0 \quad (49)$$

which is path independent. This is what is called entropy that is an exact differential

$$dS = \frac{dQ}{T} \quad (50)$$

Entropy:

Now move to the first law of thermodynamics:

$$\begin{aligned} dU &= dQ + dW = dQ - PdV \\ \Rightarrow dQ &= dU + PdV = C_V dT + PdV \\ \Rightarrow dS &= \frac{dQ}{T} = C_V \frac{dT}{T} + \frac{P}{T} dV = C_V \frac{dT}{T} + Nk_B \frac{dV}{V} \end{aligned} \quad (51)$$

To obtain entropy we can calculate the change as

$$\Delta S = C_V \ln \left(\frac{T_f}{T_i} \right) + Nk_B \ln \left(\frac{V_f}{V_i} \right) \quad (52)$$

On the other hand, we revisit again the first law of thermodynamics. For a reversible process we know that $dQ = TdS$ and $dW = -PdV$ and thus

$$\begin{aligned} dU &= dQ - PdV \\ \Rightarrow dU &= TdS - PdV \end{aligned} \tag{53}$$

Note that we can only calculate the change in entropy in such processes with the above relations.

Reversibility and Irreversibility:

As I have stressed above, it is a fact of life that some processes can occur in one direction and one direction only! Almost every process that we see around us is irreversible. This is indeed common experience - but let's be a bit more careful here. Just what does the word "irreversible" mean - especially when we use it in the context of the second law? To understand this clearly, let me start with an example of a process that you will all agree can not be reversed - the flow of heat from a hot body to a cold one when they are brought in thermal contact.

If we bring the two bodies in thermal contact for a while before separating them once again, the hotter body will lose some heat and the colder one will gain the same amount (assuming that any heat losses are negligible). When we say that this process is irreversible, does that mean that the two bodies can not be restored to their initial states? That, of course, can not be true! We can always run a refrigerator between the two bodies and take away from the colder body the amount of heat it had gained, thus restoring it to its initial state. This is not enough to restore both bodies to their initial states, though! In order to run the refrigerator, work must be done on it and hence the amount of heat it releases to the hotter body is more than the amount that was drawn out from the colder body in the first place. So, the hotter body lands up gaining more internal energy than it had started out with and our objective has not yet been achieved. But if all we wanted to do was to get the bodies back where they were, all I have to do is to bring the hot body in thermal contact with some other, colder body for a controlled period of time so that it manages to lose just the extra heat. So, there you are - both the bodies are back at their initial states, and we have managed to "reverse" an irreversible process! The sense in which this process is irreversible runs deeper, then, than merely the issue of whether the system can be restored to its initial state. Think about

what has happened to the rest of the world in our attempts to “reverse” the flow of heat. One obvious aftereffect is that the third body that we had to use has heated up. Not only that, something had to do work on the refrigerator in order to run it - so effectively, somewhere, some weight has been lowered. So, although our system is back in its initial state, we have a weight which is lower than where it was before, and a third body which is hotter than before.

For a reversible process we understood that

$$S(B) - S(A) = \int_A^B \frac{dQ_{\text{Rev.}}}{T} \quad (54)$$

For a adiabatic process the change in heat is zero meaning $dQ_{\text{Rev.}} = 0$, thus the change in entropy is also zero. The adiabatic process does not involve any entropy change i.e., isentropic process.

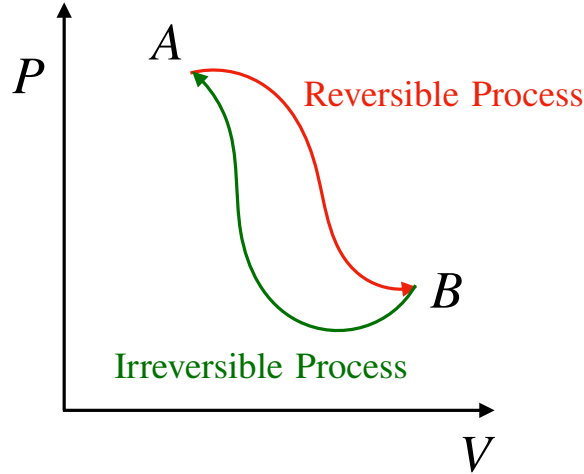


Figure 7: A cyclic process made of reversible and irreversible processes.

Let's consider we go through a cyclic process that is composed of a reversible process and irreversible process. The Clausius inequality says:

$$\begin{aligned} \oint \frac{dQ}{T} &\leq 0 \\ \Rightarrow \int_A^B \frac{dQ_{\text{Rev}}}{T} + \int_B^A \frac{dQ_{\text{Irrev}}}{T} &\leq 0 \\ \Rightarrow \int_B^A \frac{dQ_{\text{Irrev}}}{T} &\leq \int_B^A \frac{dQ_{\text{Rev}}}{T} \end{aligned} \quad (55)$$

Now the state function entropy which is exact differential, we find that

$$dS = \frac{dQ_{\text{Rev}}}{T} \geq \frac{dQ_{\text{Irrev}}}{T} \quad (56)$$

In a thermally isolated system where $dQ = 0$, we find

$$dS \geq 0 \quad (57)$$

This is another version of second law of thermodynamics. But what happens if the system is not isolated. Well, one can always think that the total entropy of the system and surroundings (the total is isolated) must increase, however, the entropy of the system can decrease.

Third law of thermodynamics:

From the second law of thermodynamics we have for a reversible and cyclic process:

$$dS = \frac{dQ}{T} \quad (58)$$

This actually defines the change in entropy in a thermodynamical process. However, it is not clear how to obtain the entropy of a specific thermodynamic state. In order to know that we must know the entropy at a time before that. This is where the third law of thermodynamics comes in. To illustrate we find the integration as

$$S(B) = S(A) + \int_A^B \frac{dQ}{T} \quad (59)$$

The third law calculates the entropy $S(A)$ such that we can obtain $S(B)$. There are several forms of this third law.

The entropy of all systems in internal equilibrium is the same at absolute zero, and may be taken to be zero. This means

$$S \rightarrow 0 \text{ at } T \rightarrow 0 \quad (60)$$

Thermodynamic Potentials:

We can define several thermodynamic energies. In fact we have already seen the energy in terms of internal energy (U), work (W) and heat (Q). However, we see that there are many processes that often happens at constant pressure, volume and

temperature. Therefore, there are other ways which can be convenient to introduce all the energies of a system.

Enthalphy:

Constant-pressure processes occur quite often, both in the natural world and in the laboratory. Instead of always talking about the energy content of a system, we can agree to always add in the work needed to make room for it (under a constant pressure, usually 1 atm). This work is PV , the pressure of the environment times the total volume of the system (that is, the total space you would need to clear out to make room for it). The enthalphy is considered as

$$H = U + PV \quad (61)$$

To create a rabbit out of nothing and place it on the table, the magician must summon up not only the energy U of the rabbit, but also some additional energy, equal to PV , to push the atmosphere out of the way to make room. The total energy required is the enthalpy, $H = U + PV$.

Let's consider the Enthalphy:

$$dH = dU + PdV + VdP \quad (62)$$

Now we know that of course:

$$dU = TdS - PdV \quad (63)$$

Inserting this into previous

$$\begin{aligned} dH &= TdS - PdV + PdV + VdP \\ \Rightarrow dH &= TdS + VdP \end{aligned} \quad (64)$$

Therefore, H is an exact differential where $H(S, P)$ such that

$$T = \left(\frac{\partial H}{\partial S} \right)_P ; \quad V = \left(\frac{\partial H}{\partial P} \right)_S \quad (65)$$

Helmholtz Free Energy:

Often, however, we're not interested in the total energy needed or the total energy that can be recovered. If the environment is one of constant temperature, the system can extract heat from this environment for free, so all we need to provide, to

create the system from nothing, is any additional work needed. And if we annihilate the system, we generally can't recover all its energy as work, because we have to dispose of its entropy by dumping some heat into the environment. So I'd like to introduce one more useful quantities that are related to energy and analogous to H . One is the Helmholtz free energy,

$$F = U - TS \quad (66)$$

The total energy that is required to create a system out of nothing is the internal energy of the system minus the heat that can be extracted from the environment for free. Therefore, such heat energies are "free" leading to the Helmholtz free energy.

For Free energy:

$$\begin{aligned} dF &= dU - TdS - SdT \\ &= TdS - PdV - TdS - SdT \\ &= -PdV - SdT \end{aligned} \quad (67)$$

Therefore, F is an exact differential where $F(V, T)$ such that

$$P = - \left(\frac{\partial F}{\partial V} \right)_T ; \quad S = - \left(\frac{\partial F}{\partial T} \right)_V \quad (68)$$

Gibb's Free Energy:

The word "work" in the previous paragraph means all work, including any that is done automatically by the system's surroundings. If the system is in an environment with constant pressure P and constant temperature T , then the work you need to do to create it, or the work you can recover when you destroy it, is given by the Gibbs free energy,

$$G = U - TS + PV \quad (69)$$

To create a rabbit out of nothing and place it on the table, the magician need not summon up the entire enthalpy, $H = U + PV$. Some energy, equal to TS , can flow in spontaneously as heat; the magician must provide only the difference, $G = H - TS = U + PV - TS$, as work.

We can work out the following:

$$\begin{aligned} dG &= dU - TdS - SdT + PdV + VdP \\ &= TdS - PdV - TdS - SdT + PdV + VdP \\ &= -SdT + VdP \end{aligned} \quad (70)$$

Therefore, G is an exact differential where $G(T, P)$ such that

$$S = - \left(\frac{\partial G}{\partial T} \right)_P ; \quad V = \left(\frac{\partial G}{\partial P} \right)_T \quad (71)$$

Legendre Transformation

Even though we have physically understood how the different thermodynamic potentials arise. The potentials can also be constructed mathematically simply from first and second law of thermodynamics by means of Legendre transformation.

For an exact differential, we can write:

$$\begin{aligned} df &= \left(\frac{\partial f}{\partial x} \right)_y dx + \left(\frac{\partial f}{\partial y} \right)_x dy \\ &= u dx + v dy \end{aligned} \quad (72)$$

We know that u and x are conjugate pair of variables and similarly v and y . We could construct two differentials:

$$d(ux) = x du + u dx \quad (73)$$

$$d(vy) = y dv + v dy \quad (74)$$

The subtraction provides:

$$df - d(ux) = d(f - ux) = v dy - x du \quad (75)$$

$$df - d(vy) = d(f - vy) = u dx - y dv \quad (76)$$

This is exactly the Legendre transformation provides.

Now we are ready to construct the other potentials. The two thermodynamical law combines as

$$dU = T dS - P dV \quad (77)$$

Here, comparing we find:

$$f = U; \quad x = S; \quad y = V; \quad u = T; \quad v = -P \quad (78)$$

Following the Legendre transformation we find

$$\begin{aligned} d(f - ux) &= d(U - TS) = -P dV - S dT = dF \\ d(f - vy) &= d(U + PV) = T dS + V dP = dH \end{aligned} \quad (79)$$

Maxwell's relations

These are required to calculate and relate different energy potentials. These are mostly mathematical exercises.

We know that the exact differentials are not path dependent meaning that in a closed loop the function must be zero. These are irrotational which means for a function $f(x, y)$

$$\begin{aligned}\nabla \times \nabla f &= 0 \\ \Rightarrow \nabla \times \left[\frac{\partial f}{\partial x} \Big|_y \hat{\mathbf{x}} + \frac{\partial f}{\partial y} \Big|_x \hat{\mathbf{y}} \right] &= 0 \\ \Rightarrow \frac{\partial^2 f}{\partial x \partial y} &= \frac{\partial^2 f}{\partial y \partial x}\end{aligned}\tag{80}$$

This is exactly the essence of Maxwell's relations.

Internal Energy:

$$dU = TdS - PdV\tag{81}$$

$$T = \left(\frac{\partial U}{\partial S} \right)_V; \quad P = - \left(\frac{\partial U}{\partial V} \right)_S\tag{82}$$

As dU is an exact differential, following the Maxwell's relation can be written

$$\frac{\partial^2 U}{\partial S \partial V} = \frac{\partial^2 U}{\partial V \partial S} \Rightarrow \left(\frac{\partial P}{\partial S} \right)_V = - \left(\frac{\partial T}{\partial V} \right)_S$$

Enthalpy:

$$dH = TdS + VdP\tag{83}$$

$$T = \left(\frac{\partial H}{\partial S} \right)_P; \quad V = \left(\frac{\partial H}{\partial P} \right)_S\tag{84}$$

As dH is an exact differential, following the Maxwell's relation can be written

$$\frac{\partial^2 H}{\partial S \partial P} = \frac{\partial^2 H}{\partial P \partial S} \Rightarrow \left(\frac{\partial V}{\partial S} \right)_P = \left(\frac{\partial T}{\partial P} \right)_S$$

Helmholtz:

$$dF = -PdV - SdT \quad (85)$$

$$P = -\left(\frac{\partial F}{\partial V}\right)_T; \quad S = -\left(\frac{\partial F}{\partial T}\right)_V \quad (86)$$

As dF is an exact differential, following the Maxwell's relation can be written

$$\frac{\partial^2 F}{\partial V \partial T} = \frac{\partial^2 F}{\partial T \partial V} \Rightarrow \left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$

Gibbs:

$$dG = VdP - SdT \quad (87)$$

$$V = \left(\frac{\partial G}{\partial P}\right)_T; \quad S = -\left(\frac{\partial G}{\partial T}\right)_P \quad (88)$$

As dG is an exact differential, following the Maxwell's relation can be written

$$\frac{\partial^2 G}{\partial P \partial T} = \frac{\partial^2 G}{\partial T \partial P} \Rightarrow \left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$$

Thermodynamic Equilibrium

Here we try to find out the equilibrium properties of a system when it is in contact with the surroundings. Let us consider that the surroundings are at a constant pressure P_0 and temperature T_0 . The first and second law of thermodynamics state that

$$dU = TdS - PdV \quad (89)$$

When the system expands and the surroundings contract by volume dV , then We find

$$\begin{aligned} -dU &= T_0 dS_0 + P_0 dV \\ \Rightarrow T_0 dS_0 &= -[dU + P_0 dV] \end{aligned} \quad (90)$$

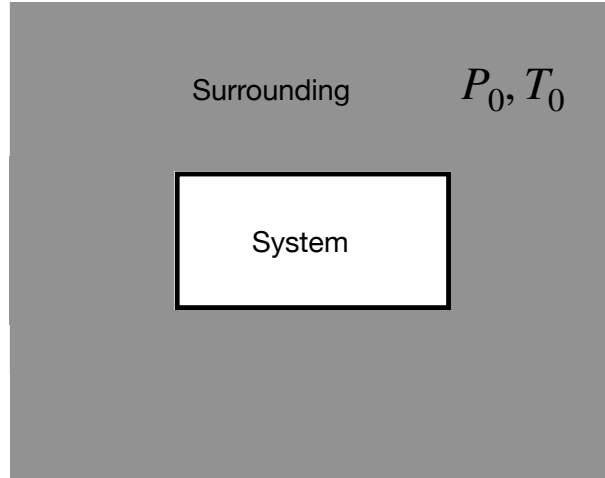


Figure 8: The system and surroundings shown where the surrounding remains at constant pressure P_0 and temperature T_0 .

This defines the change in entropy for the surroundings. However, if the change in entropy of the system is dS , then the total entropy change is

$$\begin{aligned}
 dS_{\text{tot}} &\geq 0 \\
 \Rightarrow dS + dS_0 &\geq 0 \\
 \Rightarrow -[dU + P_0 dV - T_0 dS] &\geq 0 \\
 \Rightarrow [dU + P_0 dV - T_0 dS] &\leq 0
 \end{aligned} \tag{91}$$

Define $A = U + P_0 V - T_0 S$ is thermodynamic availability function such that at constant pressure and temperature

$$dA = dU + P_0 dV - T_0 dS \tag{92}$$

$$dA \leq 0$$

This is exactly the thermodynamics equilibrium condition. The change in the availability function is negative. Such a thermodynamical process will happen spontaneously meaning that the system itself will find the equilibrium such that the system lies in the ground state. However, the other process is unlikely to happen where $dA > 0$.

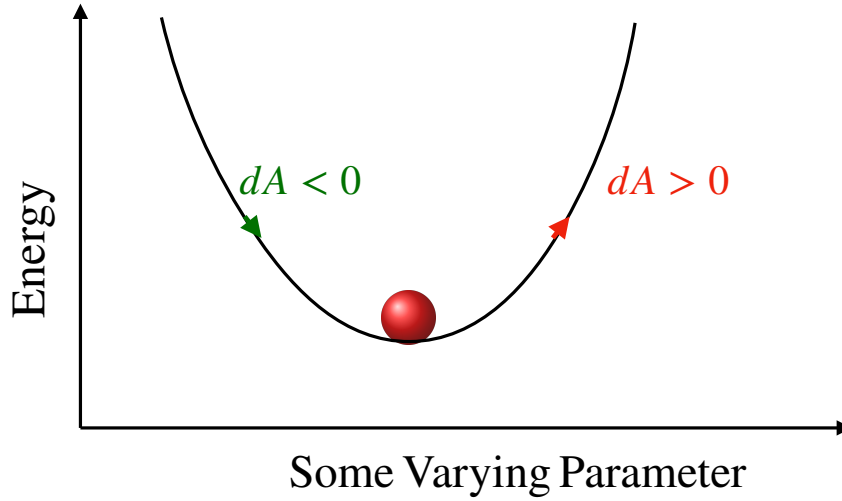


Figure 9: The system remains at equilibrium when the availability function A is minimized. In a process when $dA < 0$, the process will happen spontaneously.

Fixed Entropy and Volume: In such cases the change in internal energy is negative i.e., the internal energy must be minimised.

$$dU \leq 0 \quad (93)$$

Fixed Entropy and Pressure: In such cases the change we find

$$dA = dU + P_0 dV = dH \quad (94)$$

The enthalpy must be minimised in this cases to obtain equilibrium.

$$dH \leq 0 \quad (95)$$

Isothermal system with fixed volume: In this case, no heat transfer is allowed and the system cannot do any work thus

$$\begin{aligned} dA &= -T_0 dS \leq 0 \\ dS &\geq 0 \end{aligned} \quad (96)$$

Thus we must maximize the entropy of a isolated system to obtain equilibrium.

Fixed volume of the system and fixed temperature of the surroundings:

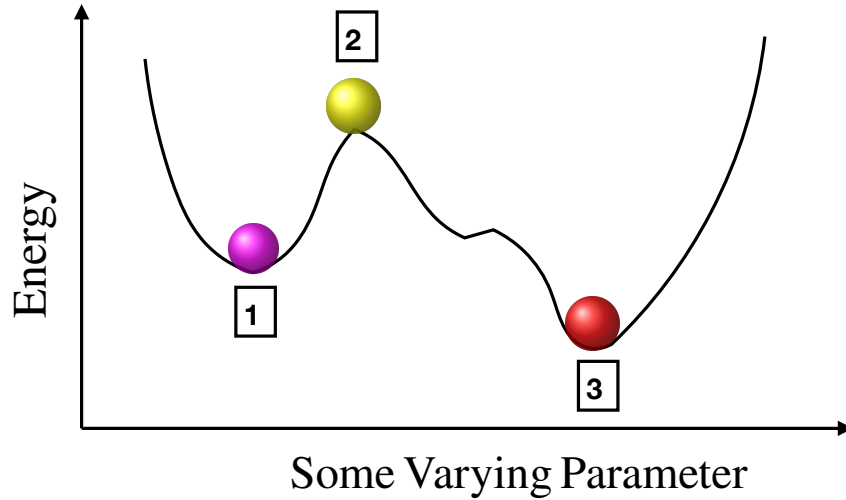
$$dA = dU - T_0 dS \leq 0 \quad (97)$$

Therefore, $dF \leq 0$ meaning the Helmholtz free energy must minimize to reach equilibrium.

Fixed pressure and temperature:

$$dA = dU + P_0 dV - T_0 dS \leq 0 \quad (98)$$

Therefore, $dG \leq 0$ meaning the Gibbs free energy must minimize to reach equilibrium.



- | | |
|---------------------------------|-----------------------------|
| 1 MetaStable Equilibrium | 3 Stable Equilibrium |
| 2 UnStable Equilibrium | |

Figure 10: Several equilibrium processes have been shown.

Ok, now we have understood the conditions for a system to reach to equilibrium. Now what happens if we perturb the system a bit.

1. **Stable Equilibrium:** The system returns to its original state after perturbation. This equilibrium is also reached when a global minima is attained.
2. **Neutral Equilibrium:** The system does not respond with all the finite variations of the parameters. The change is actually $dA = 0$.

3. **Unstable Equilibrium:** The system does not come back to its original state under perturbation. In this case the A has extrema such that $dA = 0$, however, it never returns to its original state.
4. **Metastable Equilibrium:** The system finds a local minima under perturbation, however, at a longer timescale it moves to the global minima.