

Elementary Notes on Classical Thermodynamics

It has been said over and over again that Thermodynamics is not an easy subject to learn and understand. Some students think the mathematics level required to study it is too high for them. This is probably just partly true, as much of the subject requires only derivatives (partial derivatives too) and integrals. What makes Thermodynamics not terribly intuitive is its *non-visualizability*. This means that to many thermodynamic variables and concepts it is not always easy to associate intuitive and pictorial notions. Speed, force and angular momentum in Mechanics, for instance, are easily imagined in terms of bodies moving under some form of push or pull, and rotating or spinning. Or consider how, in Electromagnetism, a field is made real by the arrangement of iron filings on a piece of paper held on a natural magnet. But what can we imagine when somebody talks about the entropy of a gas; or, what exactly is Gibbs free energy? The famous italian physicist Enrico Fermi, in his book on Thermodynamics [2], writes:

...thermodynamical results are generally highly accurate. On the other hand, it is sometimes rather unsatisfactory to obtain results without being able to see in detail how things really work, so that in many respects it is very often convenient to complete a thermodynamical result with at least a rough kinetic interpretation.

Fermi, thus, anticipates that a proper understanding of Thermodynamics implies some knowledge of Statistical Thermodynamics. In these notes we will, first, introduce briefly some key concepts of classical Thermodynamics, trying to relate their meaning to things that can be measured in experiments. A following paper will, then, try to explain the same concepts from a microscopic point of view, by using Statistical Thermodynamics.

1 The state of a system in thermal equilibrium

The key ingredients of the kind of Thermodynamics we will be dealing with are systems in thermal equilibrium. In short, we observe transformations of a system from one equilibrium state to the next, but we will be able to describe mathematically only equilibrium states, rather than the transformations themselves. So, for instance, we have some gas at a temperature T , contained in a cylinder made up of isolating material, and whose top side is a movable piston. If the piston is not moved, the gas in the cylinder will be in thermal equilibrium, because its temperature never changes, due to the isolating nature of the cylinder's walls. If some external force (a hand, for example) push the cylinder downwards, experience tells us that the gas gets heated, and the heating will go on until the piston stops. Then, after a while, convective motions within the gas will cease and a new stationary temperature is reached; the system has made the transition to a new equilibrium state. There is no much we can say in between equilibrium states, but we can measure the gas macroscopic quantities, like pressure, volume and temperature at the equilibrium states.

A system in thermal equilibrium will be characterised mathematically through a so-called *equation of state*, which links pressure, volume and temperature of the system. This equation can be generally written as:

$$f(p, V, T) = 0 \quad (1)$$

One of the better known systems in thermodynamic equilibrium is the *ideal gas*. The majority of the gases studied in introductory courses are well approximated by the ideal gas. What characterises this system is its equation of state, that can be written as follows,

$$pV = nRT \quad (2)$$

In this equation n is the number of gas moles and R is a universal constant known as *gas constant*; its value is $8.3145 \text{ JK}^{-1}\text{mol}^{-1}$.

EXAMPLE 1.

Prove that the gas constant is measured in $\text{JK}^{-1}\text{mol}^{-1}$.

Solution.

Before using the ideal gas equation to derive R 's dimensions, we need to be reminded about the various units used for the other variables in the equation. We have:

- p is measured in Pascals (Pa). Given that pressure is force divided by area, a Pa is measured in Newtons (N) divided by square meters, $\text{Pa}=\text{Nm}^{-2}$;
- V , the volume, is obviously measured in cubic meters, m^3 ;
- n is the number of moles, which we simply indicate as mol;
- T , the absolute temperature, is measured in Kelvin degrees, K.

We can now use the ideal gas equations to derive R units. First of all,

$$pV = nRT \quad \Rightarrow \quad R = \frac{pV}{nT}$$

Therefore,

$$[R] = \left[\frac{pV}{nT} \right] = \frac{[p][V]}{[n][T]} = \frac{\text{Nm}^3}{\text{m}^2\text{mol K}} = \frac{\text{Nm}}{\text{K mol}}$$

N times m equals work's unit, i.e. joules, J. Thus, eventually,

$$[R] = \frac{\text{J}}{\text{K mol}} \equiv \text{JK}^{-1}\text{mol}^{-1}$$

EXAMPLE 2 (from reference [1]).

Using equation (2) find out what pressure is exerted by 1.25 g of nitrogen gas in a flask of volume 250 mL, at 20°C .

Solution.

The pressure is readily obtained by re-arranging equation (2):

$$p = \frac{nRT}{V}$$

Now, 1 mol of nitrogen gas (whose formula is N_2) has a molar mass equal to 28.02 g mol^{-1} . Therefore 1.25 g of this gas corresponds to $1.25/28.02=0.04461 \text{ mol}$. Also, given that 1L equals a volume of $1\text{dm}^3=10^{-3}\text{m}^3$, 250 mL equals $250 \times 10^{-6}\text{m}^3$. To finish, if we assume that the absolute zero lies at -273°C , 20°C correspond to 293 K. Replacing all these numbers into the above equation, we obtain:

$$p = \frac{0.04461 \times 8.3145 \times 293}{250 \times 10^{-6}} = 434717\text{Pa} \approx 435\text{kPa}$$

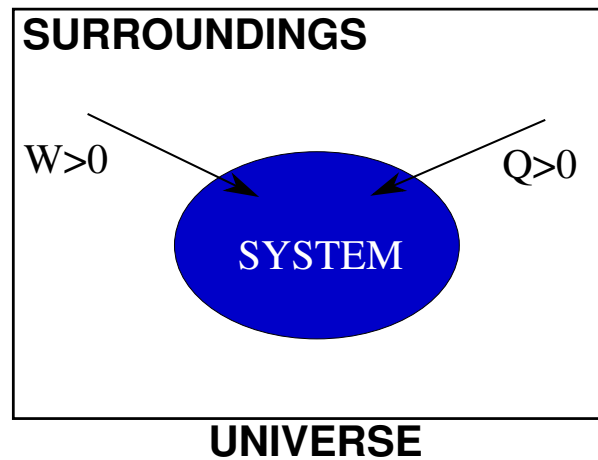


Figure 1: Thermodynamics system + surroundings. Conventions are normally adopted to define the sign of work done on the system and heat received by the system; we will define them both as positive.

2 The first law of Thermodynamics

Thermodynamics has a wide scope because the concept of thermodynamic system is a very general one. We can basically assume that any object, or group of objects, that can be separated well enough from the rest of the universe, forms a *system*. Once a system is defined, the rest of the universe is automatically defined as the *surroundings* (see Figure 1). System and surroundings form the whole of the universe:

$$\text{SYSTEM} + \text{SURROUNDINGS} = \text{UNIVERSE}$$

The system can exchange energy with the surroundings. This energy can be exchanged as either work or heat. A convention is normally adopted to define the sign of both work and heat. We will follow a definition according to which the heat received by the system, and the work done by the surroundings on the system are both positive quantities. Why do we need this convention? Because we have to balance these quantities to find out whether energy has been gained or lost by the system. The energy of the universe is conserved, it is a constant quantity; therefore if the system increases its energy, this has to be provided by the surroundings, either as heat or work. This is, in a nutshell, the *first law of Thermodynamics*,

the variation of energy of a system, due to the exchange of heat and work with the surroundings, has to balance the variation of energy of its surroundings, so that the energy in the universe is left unchanged

If we indicate with ΔU the variation of system energy, then the first law can be quantitatively expressed as,

$$\Delta U = Q + W \tag{3}$$

Some few words on the nature of the heat received by the system are needed here. In Mechanics we have been used to consider work as a vehicle to carry energy. For instance, work can be done to raise a stone from the sea level to a 100 meters; as a consequence the stone has now a potential energy higher than before. A further proof that work is energy comes from its measure units, that is joules. Heat is, as far as we know, measured in calories (cal). It was once believed to be a sort of fluid. But a brilliant series of experiments by James Joule at the beginning of the nineteenth

century established, beyond any doubt, that heat is another vehicle for energy. It, too, should be measured in joules. In fact Joule found the energy equivalent of a calorie,

$$1 \text{ cal} = 4.186 \text{ J} \quad (4)$$

Let us, now, briefly comment equation (3). That equation is about energy change. We can think of the system as possessing a certain amount of energy due to various processes which are taking place inside it. It is important to understand that in Thermodynamics we are not interested to the energy acquired or lost by the system as a consequence of overall rotational or translational motion; this is, really, the realm of Mechanics. We can rather talk of an *internal energy* that the system has as a result of the numerous micro-processes happening inside it. We do not need to be concerned with the exact nature of these processes, as this would require a deepening of the molecular nature of the system (and thus an exploration of Statistical Thermodynamics). We can be happy enough by thinking of a system as possessing internal energy, U , whose variation obeys equation (3). In this way we will never know the exact value of U in the system, but this is of no interest to us, as only energy variations can be measured by thermodynamic experiments.

EXAMPLE 3 (from reference [1]).

Nutritionists are interested in the use of energy by the human body, and we can consider our own body as a thermodynamic system. Calorimeters have been constructed which can accommodate a person to measure (nondestructively) their net energy output. Suppose in the course of an experiment a person does 622 kJ of work on an exercise bicycle and loses 20 kcal of energy as heat. What is the change in internal energy of the person?

Solution.

The first thing to do is to translate calories into joules. Using equation (4),

$$4.186 \frac{\text{J}}{\text{cal}} \times 20 \times 10^3 \text{ cal} = 83.72 \text{ kJ},$$

i.e. 20 kcal are equivalent to 83.72 kJ. The system (the person who is cycling) is doing work, not receiving work. Therefore, using our sign convention, $W = -622 \text{ kJ}$. Also the heat is given to the surroundings, so that $Q = -83.72 \text{ kJ}$. Through equation (3) we can calculate the variation in internal energy of the human body,

$$\Delta U = -622 - 83.72 = -705.72$$

as being -705.72 kJ. Thus the person's internal energy decreases of 705.72 kJ.

The internal energy is a *state property* of the system. It does not depend on how the system evolved into a given state (how it was prepared). The same cannot be said, for example, of the work and heat received by the system. These are quantities depending very much on the way the system was taken to a given state. For instance, a gas inside a cylinder could go from state (p_1, V_1, T_1) to state (p_2, V_2, T_2) by maintaining a constant volume (that is, only heat is exchanged with the surroundings) until the very end of the transformation, by insulating the cylinder to avoid heat to be exchanged with the surroundings (adiabatic transformation, only work is exchanged with the surroundings), or with a combination of the previous two transformations. We can clearly see how the system is taken to the same final state (p_2, V_2, T_2) by providing different amounts of work and heat. This difference in behaviour between the internal energy on one side, and work and heat on the other, is mathematically described when variations of these quantities are considered. The first law of Thermodynamics will, then, be written as,

$$dU = \delta Q + \delta W \quad (5)$$

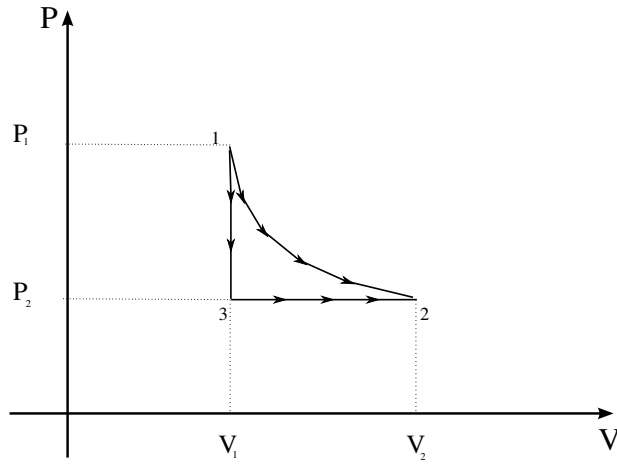


Figure 2: Two different paths are followed to take an ideal gas from state (p_1, V_1) to state (p_2, V_2) . The first corresponds to an isotherm transformation and, in the picture, goes from 1 straight to 2. The second is made up of two separate transformations, one going from 1 to 3 (isochoric) and one going from 3 to 2 (isobaric).

and both the d and δ symbols will indicate infinitesimal variations, and therefore follow the standard rules of differential calculus, but δ will point out to a variation depending on the way the transformation is carried out. A simple quantitative example of what has just been said can be made using reversible transformations in an ideal gas [3] (see Figure 2). Let us consider the gas enclosed in the usual cylinder with the piston. At the beginning the state is described by pressure p_1 , volume V_1 and temperature $T_0 \equiv p_1 V_1 / (nR)$, as given by the equation of state. The gas can, then, transform to a final state (p_2, V_2, T_0) in two ways, either with an isotherm (constant temperature) transformation, or with the combination of an isochoric (constant volume) and an isobaric (constant pressure) transformation where the intermediate temperature varies, but reaches a final value T_0 . In both cases, the infinitesimal work done by the surroundings on the system has to be defined as a positive quantity (remember our convention). Now, when the gas expands its infinitesimal volume variation is a positive quantity. The surroundings volume variation is, correspondingly, a negative quantity. Thus, given that pressure is a positive quantity, the infinitesimal work has to be defined as,

$$\delta W = -pdV \tag{6}$$

We can, at this point, calculate the work for both transformations. For the isothermal one,

$$W_A = - \int_{V_1}^{V_2} p dV = -nRT_0 \int_{V_1}^{V_2} \frac{dV}{V} = -nRT_0 \ln \left(\frac{V_2}{V_1} \right)$$

A different value for the work taking the gas from 1 to 2 is obtained by the isochoric + isobaric transformations,

$$W_B = - \int_{V_1}^{V_1} p dV - \int_{V_1}^{V_2} \frac{nRT_0}{V_2} dV = 0 - nRT_0 \frac{V_2 - V_1}{V_2} = -nRT_0 \frac{V_2 - V_1}{V_2}$$

where we have used, again, the equation of state to calculate the final pressure as nRT_0/V_2 . Given that $\ln(V_2/V_1) \neq (V_2 - V_1)/V_2$, we easily deduce that $W_A \neq W_B$. We should not be surprised to find here a negative value for work; in an expansion from volume V_1 to volume V_2 the gas is actually doing work on the surroundings and, due to our convention, this work has to be considered as negative because it takes internal energy away from the system.

3 Heat capacity

So far we have introduced heat as a quantity related to energy, but we have spent not many words on it. We relate heat to our sensory perception of hot and cold objects, but we need an objective way of measuring it. An interesting and important physical observation which comes into place here is that if we provide an equal amount of heat to two bodies with same volumes but different materials, then the increase of temperature will in general be different in the two bodies. The same can be observed with bodies of a same material but with different volumes. We could, then, use such a temperature variation to have a quantitative measure of the heat administered to a body. In order to do so we will need to choose a representative substance and certain fixed conditions that are easily reproducible. This is, in truth, how the calorie is defined; it is the amount of heat needed to increase the temperature of a gram of pure water, at atmospheric pressure, from 14°C to 15°C. The heat over temperature ratio, which is a key factor in the definition of heat measuring unit, is an important quantity in Thermodynamics. In general, the *heat capacity* (or *thermal capacity*) of a body is, by definition, the ratio ($\delta Q/dT$) between an infinitesimal quantity of heat absorbed by the body and the related, infinitesimal increase of its temperature. When the temperature changes its value the system changes its state. The heat dispersed or absorbed in this process depends, as we have seen, on the specific way in which the transformation has occurred. It is of no surprise, then, to discover that the heat capacity will be different according as to whether the body is heated at constant volume or at constant pressure; heat capacities corresponding to these two cases will be denoted, respectively, as C_V and C_p . Through the mathematical expression of the first law of Thermodynamics, heat capacities can be related to the internal energy. Let us consider the usual gas example, with work expressed as $\delta W = -pdV$,

$$dU = \delta Q - pdV$$

If we choose V and T as the independent variables (remember that the three variables defining the gas' state are not all independent, due to the equation of state), then U will depend on them and,

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

where the subscripts outside the parenthesis indicate that the variations are performed with that particular variable kept constant. By replacing this last expression for dU in the previous one we obtain,

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

or,

$$\delta Q = \left(\frac{\partial U}{\partial T}\right)_V dT + \left[p + \left(\frac{\partial U}{\partial V}\right)_T\right] dV \quad (7)$$

An expression of heat capacity at constant volume can now be readily obtained by using its definition and relation (7),

$$C_V \equiv \left(\frac{\delta Q}{dT}\right)_{dV=0} = \left(\frac{\partial U}{\partial T}\right)_V \frac{dT}{dT}$$

Thus,

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \quad (8)$$

The expression for the heat capacity at constant pressure can be derived in a similar way. The final result is,

$$C_p = \left(\frac{\partial U}{\partial T}\right)_p + p \left(\frac{\partial V}{\partial T}\right)_p \quad (9)$$

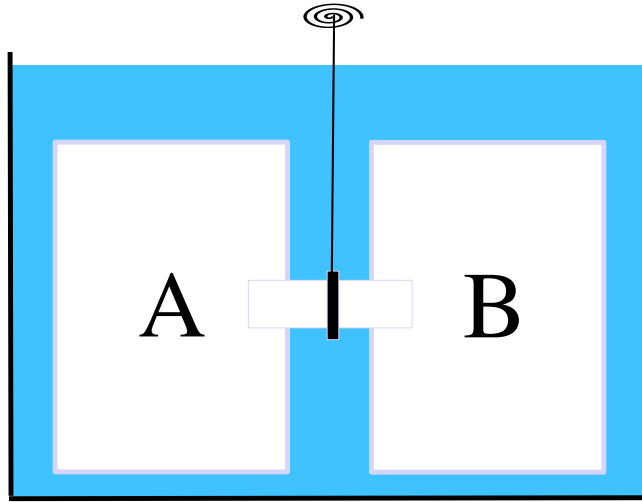


Figure 3: Schematic diagram showing Joule experiment for proving that $U = U(T)$ for an ideal gas.

EXAMPLE 4.

Prove that, for an ideal gas, the difference between heat capacities at constant pressure and volume equals the gas constant, i.e.,

$$C_p - C_V = R \quad (10)$$

Solution.

In order to prove this important result we have to introduce, first, another key feature of ideal gases:

for an ideal gas the internal energy depends only on temperature

Although the above finding can be rigorously proved using the second law of Thermodynamics, we will introduce it using a simplification of an experiment actually performed by Joule (see Figure 3). Two containers, A and B, connected by a pipe are immersed in the water of a calorimeter. At the beginning of the experiment a certain amount of gas fills completely chamber A. The gas cannot diffuse through to chamber B because of a stopcock in the connecting tube. After the gas in A has settled, and the whole system has reached thermal equilibrium, the stopcock is opened and the gas is allowed to flow freely from A to B. We wait until the system settles to a new thermal equilibrium and then measure any temperature change. No variation in temperature is observed, i.e. the heat given or absorbed by the A+B system is null. Using the first law of Thermodynamics, equation (3), we deduce that,

$$\Delta U = W$$

At the beginning of the experiment the volume of the whole system is $V_A + V_B$ because, although the gas was initially contained only in A, yet the whole A+B system is contained in the calorimeter. At the end of the experiment the volume is still $V_A + V_B$, i.e. it is unchanged. Therefore the system has done no work on the surroundings and vice versa, $W = 0$. The first law turns thus into,

$$\Delta U = 0$$

The above equation means that the internal energy (due to all molecules of the gas) has not changed. If we, now, focus on the gas we can notice that a change in the gas volume (from V_A to $V_A + V_B$) has no bearings on its internal energy. Before the experiment was performed we might have assumed, quite generally, that the internal energy of the gas depended on two variables (the

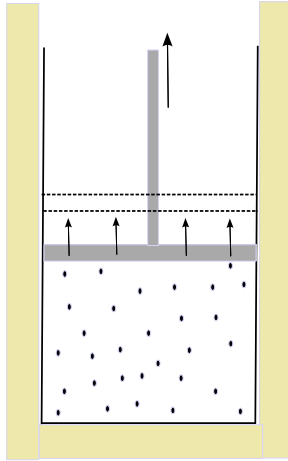


Figure 4: Adiabatic expansion of an ideal gas in a thermally insulated cylinder.

third is constrained by the gas equation), say T and V . But, given that no change in internal energy is observed for a change in volume, we deduce that the internal energy does not depend on V , $U = U(T)$: the energy of an ideal gas is a function of the temperature only. Let us now proceed to prove what the problem asked as to do. Using relation (8) (without V subscript given that, as we have just seen, U depends on T only) in the first law we have,

$$dU = \delta Q - pdV \quad \Rightarrow \quad \delta Q = C_V dT + pdV \quad (11)$$

Let us now consider the equation of an ideal gas for one mole of substance,

$$pV = RT$$

and let us differentiate it,

$$pdV + Vdp = RdT$$

Replacing this in (11) we get:

$$\begin{aligned} \delta Q &= C_V dT + RdT - Vdp \\ &\Downarrow \\ \delta Q &= (C_V + R)dT - Vdp \end{aligned} \quad (12)$$

By definition, $C_p = (\delta Q/dT)_p$, where the subscript means that there is no pressure variation, $dp = 0$. From equation (12) we obtain, then,

$$C_p = C_V + R$$

which is what we wanted to prove.

4 The adiabatic transformation

In an *adiabatic* transformation there is neither heat transmission nor heat absorption, the system is thermally insulated. In order to find out how pressure and volume are related in an adiabatic transformation, let us focus on an adiabatic gas expansion (see Figure 4). To avoid heat exchange with the surroundings, the gas can be considered enclosed in a cylinder whose walls are thermally insulated. At the beginning the gas, at temperature T_{ini} , fills a volume V_{ini} ; after the expansion

has taken place the volume is $V > V_{ini}$, and the new temperature is T . We can use equation (11) to re-write the first law:

$$\delta Q = C_V dT + p dV$$

Now, the heat exchanged at any little step of the expansion is null, because this is adiabatic. Also, we can eliminate p through the equation of state (which is supposed to hold at any time during the transformation). Thus, the previous relation becomes,

$$C_V dT + RT \frac{dV}{V} = 0$$

where only one mole of gas is being considered. Finally, by dividing both members by $C_V T$, we get

$$\frac{dT}{T} + \frac{R}{C_V} \frac{dV}{V} = 0$$

The gas constant is given by $C_p - C_V$ so that the quantity R/C_V becomes $C_p/C_V - 1$. It is customary to call $\gamma \equiv C_p/C_V$. Therefore the previous equation is re-written as,

$$\frac{dT}{T} + (\gamma - 1) \frac{dV}{V} = 0 \quad (13)$$

The above equation is readily integrated, between T_{ini} and T and between V_{ini} and V , to give,

$$\begin{aligned} \ln \left(\frac{T}{T_{ini}} \right) + (\gamma - 1) \ln \left(\frac{V}{V_{ini}} \right) &= \text{const} \\ \Downarrow \\ \ln \left(\frac{T}{T_{ini}} \right) + \ln \left(\frac{V}{V_{ini}} \right)^{(\gamma-1)} &= \text{const} \\ \Downarrow \\ \ln \left[\frac{T}{T_{ini}} \left(\frac{V}{V_{ini}} \right)^{(\gamma-1)} \right] &= \text{const} \end{aligned}$$

Eventually, taking the exponential of both sides,

$$TV^{(\gamma-1)} = \text{const} \quad (14)$$

Equation (14) is what we were looking for. Sometimes it is better to express the same transformation using pressure and volume, rather than temperature and volume. Using $T = pV/R$ in the above equation leads us to:

$$pV^\gamma = \text{const} \quad (15)$$

with $\gamma > 1$, given that C_p is always larger than C_V . The difference between an isotherm, $pV = \text{const}$, and an adiabatic, $pV^\gamma = \text{const}$, transformation is the γ , a number always greater than 1. So, in a (p, V) diagram, the curves describing an adiabatic transformation will always be similar to hyperbolae, like the isotherms, but slightly steeper, due to γ (see Figure 5 for an example of that).

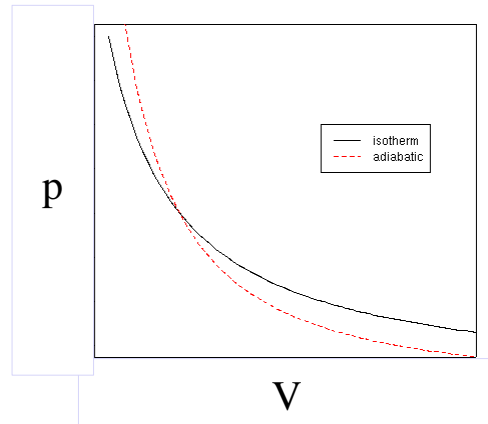


Figure 5: In this (p, V) diagram the full line corresponds to an isotherm transformation, $pV = \kappa$, while the dotted line corresponds to an adiabatic transformation, $pV^\gamma = \kappa$, with $\gamma = 1.5$. The adiabatic curve is markedly steeper than the isotherm one.

5 The efficiency of engines

The first law of Thermodynamics tells us that in any process the energy is conserved. We can convert heat into work, but during the process no further energy is created or lost. Scientists have been, and still are, particularly interested in how well a given quantity of heat can be transformed into useful work. Experience tells us that some, or a lot of, heat is never converted into work. This is where the second law of Thermodynamics comes into play. It has to do with engines (which convert heat into work and vice-versa) and their efficiencies. It is important that we define the concept of efficiency before discussing the second law in all its aspects.

A generic engine is an apparatus which operates between two heat reservoirs at two different temperatures, and which absorbs heat to produce some work (see Figure 6). The engine itself can be roughly identified with a substance operating in a cycle, i.e. the initial and final state of

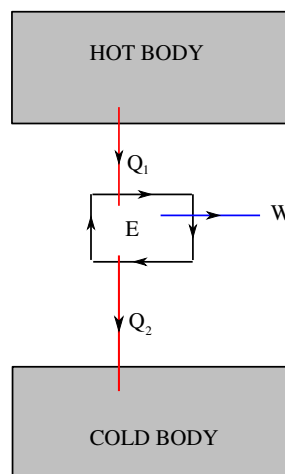


Figure 6: Schematic representation of a generic engine. The engine E works by absorbing a quantity of heat Q_1 from a hot reservoir, by producing work W and rejecting a quantity of heat Q_2 into a cold reservoir.

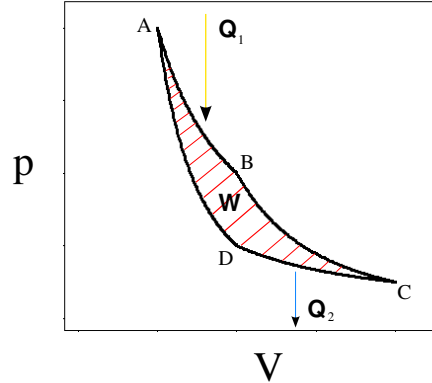


Figure 7: The Carnot cycle. During one cycle the engine has done positive work on the surroundings, equivalent to the shaded area.

this substance are the same. If W is the amount of work produced by the engine (according to our previous sign convention, $-W$ is the work done by the surroundings on the engine), and if Q_1 heat is absorbed from an hot reservoir, while Q_2 heat is released to the cold reservoir, then the variation of internal energy of the engine is:

$$\Delta U = Q_1 - Q_2 - W$$

Given that the substance forming the engine operates in a cycle, the internal energy of the initial state is equal to the internal energy of the final state; it follows that $\Delta U = 0$. From the previous equation we obtain, thus, an important result,

$$W = Q_1 - Q_2, \tag{16}$$

i.e. the work produced by an engine is equivalent to the difference between the heat absorbed and the heat released to the reservoirs. To measure how well a certain amount of heat is transformed into work, or how well work is transformed into heat, the ratio between work done over heat absorbed is used. More specifically, using the notation previously introduced, the *efficiency* η of the engine is defined as:

$$\eta \equiv \frac{W}{Q_1} \tag{17}$$

or, using equation (16),

$$\eta = 1 - \frac{Q_2}{Q_1} \tag{18}$$

Quite often the efficiency is expressed as a percentage, i.e. the definition of equation (18) is multiplied by 100.

Among the many engines created by engineers or that can be designed, the *Carnot engine* plays a fundamental role in Thermodynamics. This is defined as any engine that operates between only two reservoirs and it is reversible, meaning that if the engine inverts its cycle, it will go through the same steps as in the direct cycle. The Carnot engine is made up of four transformations, two isotherms and two adiabatics, according to the scheme in Figure 7. The substance forming the essential part of the engine starts at volume V_A and temperature T_1 . Then it undergoes an isotherm expansion up to volume V_B , by accepting an amount of heat Q_1 . At this point the system is thermally insulated and the expansion continues to volume V_C ; this is, obviously, an

adiabatic expansion, where the temperature drops to T_2 . Now the compression part of the engine starts. First we have an isotherm compression, where heat Q_2 is expelled. Then an adiabatic compression, where the temperature raises again to the original value T_1 . After this the cycle is repeated identically. As we know, in a (p, V) diagram the work is equivalent to the area under the curve representing each transformation. In a cycle, therefore, the work done by the system is equivalent to the area enclosed by the curves forming it. The work done by the system will be positive (i.e. the work done by the surroundings will be negative) if the cycle is run clockwise; otherwise it will be negative. We will see few applications of the Carnot cycle in the next sections.

6 The second law of Thermodynamics: postulates

It is customary to introduce the second law of Thermodynamics through the enunciation of two postulates, through the *Kelvin-Planck* and the *Clausius* statements. The reading of these, alone, is probably not sufficient to a proper understanding of the law. We will, then, need to follow up the enunciation with a qualitative discussion of the postulates' consequences.

6.1 Kelvin-Planck statement

It is impossible to construct a device that, operating in a cycle, will produce no effect other than the extraction of heat from a single body at a uniform temperature and the performance of an equivalent amount of work

The above passage can, perhaps, be understood more clearly by looking at Figure 8. The engine E extracts heat from a hot reservoir, but it does not release any heat to a cold reservoir, as in a typical engine. Therefore all heat extracted will have to be converted into heat, $W = Q$. Experience tells us that such a situation never occurs in nature. An engine exchanging heat with just one reservoir can produce an amount of work always smaller than the amount of heat extracted. We can never achieve an engine so efficient as to convert all the heat into work. The engine forbidden in Kelvin-Planck's postulate has $Q_2 = 0$. Therefore, using formula (18), its efficiency is,

$$\eta = 1 - \frac{0}{Q_1} = 1$$

i.e. that would be an engine with a 100% efficiency.

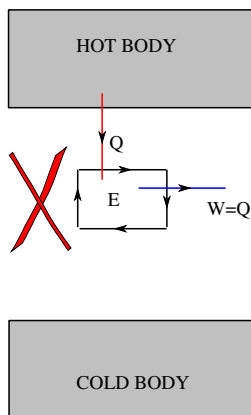


Figure 8: The second law as contained in the Kelvin-Planck statement. The kind of engine here depicted can never be realised in nature.

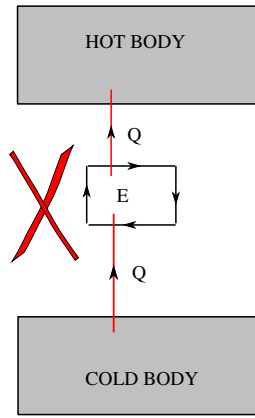


Figure 9: The second law as contained in the Clausius statement. The kind of engine here depicted can never be realised in nature.

6.2 Clausius statement

It is impossible to construct a device that, operating in a cycle, produces no effect other than the transfer of heat from a colder to a hotter body

The device described in the above passage is schematically shown in Figure 9. We never observe the spontaneous transfer of heat from a cold to a hot body. We could, in principle, design an engine for doing that; after all, every refrigerator does just that. But the kind of machine depicted in Figure 9 does not need to produce any work at all for allowing the transfer. From a first-law point of view there is no problem as the quantity of heat absorbed, $Q_1 = Q$ is equal to the quantity of heat released, $Q_2 = Q$. But Clausius statement tells us that an engine like the one just described can never be assembled. In other words, if heat has to be transferred from a cold to a hot body, then we need work to carry out this process. If we were to compute the efficiency of the engine in Figure 9 using formula (18) we would find $\eta = 0$. But this is contrary to our intuition according to which an engine extracting heat from a cold body and pumping it into a hot body (basically a refrigerator) is more efficient if it carries out little work. We could, then, adopt a different definition for the efficiency of refrigerators. There is, in fact, a quantity customarily used, known as *coefficient of performance* of a refrigerator. This is defined as:

$$\eta^R \equiv \frac{Q_2}{W} \quad (19)$$

For the engine described by the Clausius statement we have $W = 0$, $Q_2 = Q$; therefore its efficiency is infinite. This makes more sense, although we know we can never have real infinitely-efficient refrigerators.

6.3 Equivalence of Kelvin-Planck and Clausius statements

The statements we have introduced are different, but both describe forbidden situations for thermodynamic processes. In this section we are going to show that the two descriptions are, in fact, equivalent. We will proceed by proving that if one of the statements is not true, then the other one is wrong too.

Let us, first, suppose that Kelvin-Planck statement is wrong. An engine E, extracting heat Q_1 and delivering work $W = Q_1$ is, thus, possible. Close to this engine let us devise another engine, a refrigerator R, which takes heat Q_2 from the cold reservoir and releases heat $Q_1 + Q_2$ to the hot reservoir. In order to obey the first law, R needs to do negative work $W = -Q_1$. This is

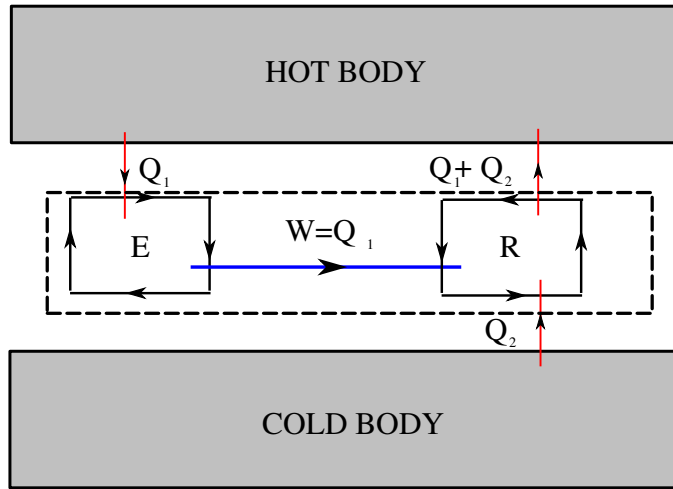


Figure 10: Composite engine to prove the equivalence of Kelvin-Planck and Clausius statements.

simply equivalent to the work provided by E (see Figure 10). If we consider the composite engine formed by E and R, we have as a result an engine which absorbs heat Q_2 from a cold reservoir and releases heat $-Q_1 + Q_1 + Q_2 = Q_2$ to a hot reservoir, without performing any work. Such an engine, though, is equivalent to the one forbidden by Clausius statement. Therefore, by assuming Kelvin-Planck not true we have to accept that Clausius is not true.

Next, let us assume Clausius statement to be false, i.e. we can build an engine R which absorbs heat Q_2 from a cold reservoir and release the same amount of heat into a cold reservoir, without the need of any work. We are free, though, to side this engine with another one extracting a quantity of heat Q_1 from the hot reservoir and returning a quantity of heat Q_2 to the cold reservoir; this engine would, then, necessarily carry out work $W = Q_1 - Q_2$ in order to obey the first law (see Figure 11). If we, now, consider the composite engine formed by R and E, we have an engine which extracts heat $Q_1 - Q_2$ from the hot reservoir, returns heat $Q_2 - Q_2 = 0$, i.e. no heat at all, to the cold reservoir, and carries out an amount of work $W = Q_1 - Q_2$. In other words, we have an engine transforming all the extracted heat into work, precisely what Kelvin-Planck statement forbids. This completes the proof that Kelvin-Planck and Clausius statements are equivalent enunciations. They are different descriptions of Thermodynamics second law.

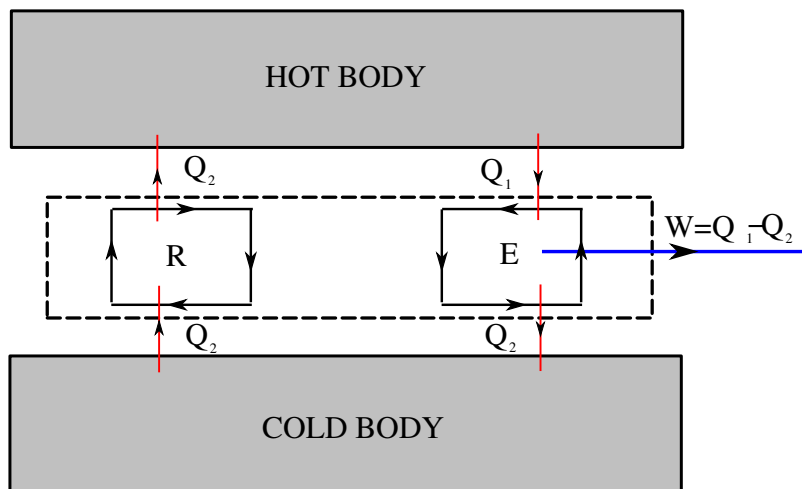


Figure 11: Composite engine to prove the equivalence of Clausius and Kelvin-Planck statements.

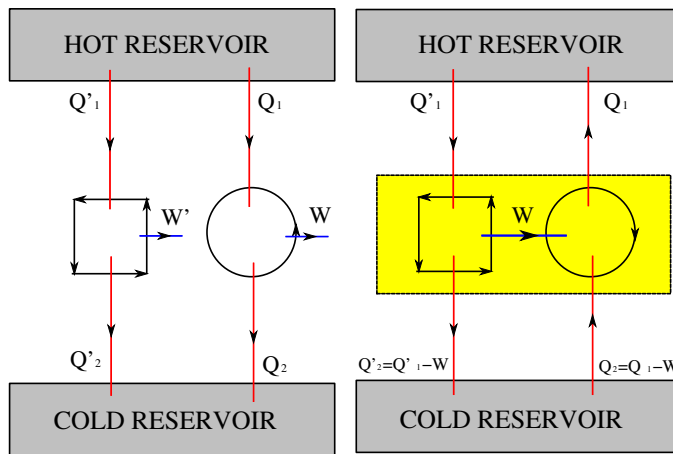


Figure 12: Composite engine to prove Carnot theorem.

7 The second law of Thermodynamics: Carnot's theorem and the absolute thermodynamic scale of temperature

With an argument similar in nature to those presented to prove the equivalence between Kelvin-Planck and Clausius statements, we can now show that

no engine operating between two reservoirs can be more efficient than a Carnot engine operating between those same two reservoirs

Let us consider, then, an hypothetical engine E operating between a hot and a cold reservoir. The engine extracts heat Q'_1 from the hot reservoir and returns heat Q'_2 to the cold reservoir performing, at the same time, work W' . Let us also consider a Carnot engine, C, operating between the same two reservoirs. It extracts heat Q_1 and returns heat Q_2 , performing work W . Let us assume, for the remainder, that the hypothetical engine has a higher efficiency than the Carnot engine. If $W' = W$:

$$\eta \geq \eta_C \quad (20)$$

Using definition (17), the above conditions leads to the following result:

$$\frac{W}{Q'_1} \geq \frac{W}{Q_1} \quad \Rightarrow \quad Q_1 \geq Q'_1$$

At this point let us reverse the cycle of C and make it act as a refrigerator (see Figure 12). Given that this refrigerator can function thanks to the work provided by E, we have a composite E+C engine which extracts heat,

$$Q_2 - Q'_2 \quad \Leftrightarrow \quad (Q_1 - W) - (Q'_1 - W) = Q_1 - Q'_1$$

from the cold reservoir and returns positive heat $Q_1 - Q'_1$ to the hot reservoir, without performing any amount of net work. But this is exactly what Clausius statements of the second law forbids. Things can be re-adjusted only if we make $Q_1 - Q'_1$ a negative or null quantity. This, in turn, means to make engine E efficiency smaller or equal to the efficiency of the Carnot engine, which is what we wanted to prove.

With an analogous argument we can easily show that any two different Carnot engines, operating between the same reservoirs, have exactly the same efficiency. So, if heat Q_1 and heat Q_2 are

respectively extracted from the hot reservoir and returned to the cold reservoir by a first Carnot engine C , while Q'_1 and Q'_2 are exchanged between the same reservoirs by another Carnot engine C' , then the previous statement is equivalent to the following relation:

$$\eta_C = \eta_{C'} \quad \Leftrightarrow \quad 1 - \frac{Q_2}{Q_1} = 1 - \frac{Q'_2}{Q'_1} \quad \Rightarrow \quad \frac{Q_2}{Q_1} = \frac{Q'_2}{Q'_1}$$

Thus, whichever amount of heat is exchanged between a hot and cold reservoir by a Carnot engine, the ratio of heat returned to heat absorbed seems to be a constant. It will, therefore, depend only on the temperatures of the two reservoirs. We can describe this mathematically with the following relation,

$$\frac{Q_2}{Q_1} = f(T_2, T_1) \quad (21)$$

where the exact analytic form of function $f(T_2, T_1)$ is, at the moment, unknown. This function, though, has a couple of interesting properties. Consider, for example, a Carnot engine working in a direct cycle. It extracts heat Q from a hot reservoir at temperature T and returns heat Q_0 to a cold reservoir with temperature T_0 . From equation (21) we have, for this engine,

$$\frac{Q_0}{Q} = f(T_0, T) \quad (22)$$

If we revert the cycle for this engine, heat Q_0 is extracted from the cold reservoir and it is transferred to the hot reservoir. In this case equation (21) reads,

$$\frac{Q}{Q_0} = f(T, T_0)$$

but, given that $Q_0/Q = 1/(Q/Q_0)$,

$$\frac{Q_0}{Q} = \frac{1}{f(T, T_0)}$$

Comparing this expression with (22) we have, as a result,

$$f(T, T_0) = \frac{1}{f(T_0, T)} \quad (23)$$

Be now C_1 a Carnot engine working between a hot and a cold reservoir at temperature T_1 and T_0 , respectively. From equation (21) it follows that,

$$\frac{Q_0}{Q_1} = f(T_0, T_1)$$

Similarly, be C_2 a Carnot engine working between temperatures T_0 and T_2 . We have:

$$\frac{Q_2}{Q_0} = f(T_2, T_0)$$

Multiplying the previous two relations we get:

$$\frac{Q_0}{Q_1} \frac{Q_2}{Q_0} = f(T_0, T_1) f(T_2, T_0)$$

or, using property (23),

$$\frac{Q_2}{Q_1} = \frac{f(T_2, T_0)}{f(T_1, T_0)} \quad (24)$$

Finally, comparing (21) with (24), we arrive at another interesting property:

$$f(T_2, T_1) = \frac{f(T_2, T_0)}{f(T_1, T_0)} \quad (25)$$

Given that temperature T_0 is totally arbitrary (we could have taken another value instead), it has to be factorized in the expressions for $f(T_2, T_0)$ and $f(T_1, T_0)$. There are not many functions like this which obey properties (23) and (25). A simple choice is the following:

$$f(T_2, T_1) = \frac{T_2}{T_1} \quad (26)$$

This is not a uniquely determined choice, given the arbitrariness of $f(T_2, T_1)$, but is a valid one and has the advantage of being quite simple; we will, then, adopt it. From (21) and (26) it immediately follows this important relation:

$$\frac{Q_2}{Q_1} = \frac{T_2}{T_1} \quad (27)$$

Through a Carnot engine and relation (27) we have established an important and objective way of measuring temperatures independently of any substance. No matter which Carnot engine is used between the two temperatures to be used, their ratio is still going to be equal to the ratio of the heat extracted. One of the two temperatures has, of course, still to be fixed arbitrarily, but this is true of any other temperature scale. The temperature scale defined in this way is known as *absolute thermodynamic scale of temperature*. The interesting thing that can be proved, but we will not carry out the demonstration here, is that the absolute scale coincides with the scale defined through an ideal gas. We do not need, then, to carry out any modification in all the equations containing T that have been previously introduced.

EXAMPLE 5.

What is the maximum efficiency of a thermal engine operating between an upper temperature of 360 °C and the lower temperature of 18 °C?

Solution.

The efficiency of any real thermal engine is smaller or equal than the efficiency of a Carnot engine operating between the same temperatures. Using equations (18) and (27), we can express this efficiency as a function of temperatures only according to,

$$\eta_c = 1 - \frac{T_{\text{lower}}}{T_{\text{upper}}}$$

The efficiency η of a real engine operating between T_{upper} and T_{lower} is smaller or equal to η_c . Therefore its maximum is $\eta_c = 1 - (18 + 273)/(360 + 273) \approx 0.540$. It is important to notice that we have used the absolute scale of temperatures here, where the absolute zero is roughly at -273 °C.

8 The second law of Thermodynamics: the concept of Entropy

There is an important inequality in Thermodynamics which goes under the name of Clausius inequality. This is key to understanding the concept of entropy. In order to introduce such inequality let us consider the complex cyclical process described as follows (see Figure 13). A system S (can be an engine or something else) works in a cyclical fashion, returning to its original state after one cycle. During each cycle the system exchanges heat with a series of reservoirs T_1 ,

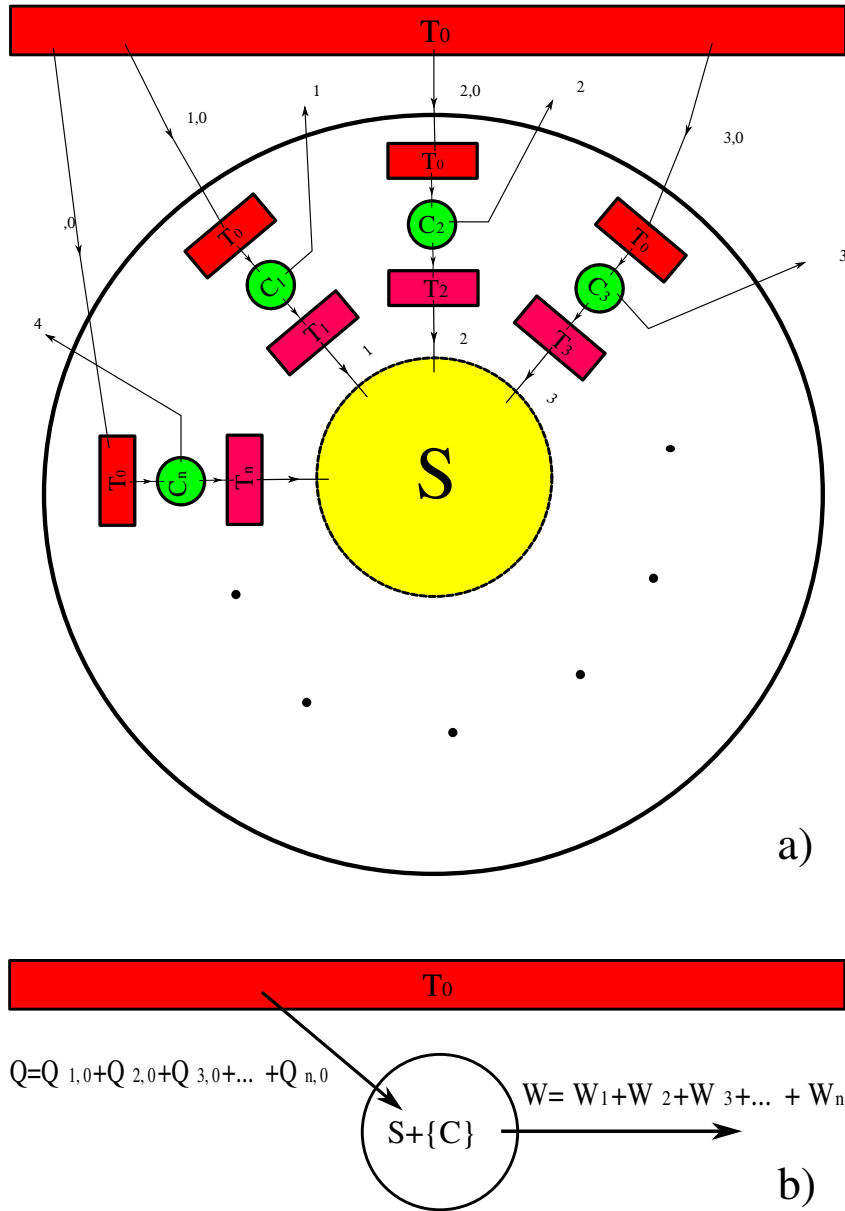


Figure 13: Composite system used to illustrate Clausius inequality. The combination of system S and a series of n Carnot machines C_i in a) is equivalent to a single system $S + C$ absorbing heat Q from the principal reservoir at temperature T_0 and returning work W , in b).

T_2, \dots, T_n . For instance, while in its state 1, it absorbs heat Q_1 from a reservoir at temperature T_1 and makes a transition to state 2. Then it absorbs heat Q_2 from a reservoir at temperature T_2 and makes a transition to state 3, and so on. Eventually, while in its state n , it absorbs heat Q_n from a reservoir at temperature T_n and makes a transition to the starting state 1. We can add to this picture a series of Carnot engines, C_1, C_2, \dots, C_n . Each engine absorbs heat from a principal common reservoir at temperature T_0 , produces work and returns heat to a different reservoir. More specifically, an engine C_i absorbs heat $Q_{i,0}$ from the principal reservoir, returns heat Q_i to the reservoir at temperature T_i , and produces some work W_i . Using equation (27), we know that $Q_i/Q_{i,0} = T_i/T_0$ and, therefore, $Q_{i,0} = T_0(Q_i/T_i)$. If we now look at the composite system, the absorbed heat is,

$$Q = \sum_{i=1}^n Q_{i,0} = T_0 \sum_{i=1}^n \frac{Q_i}{T_i}$$

while the produced work is given by the sum of all individual works by the Carnot engines:

$$W = \sum_{i=1}^n W_i$$

Given that no heat is returned to any reservoir by the composite system, we have simply,

$$W = Q$$

This means that the composite system absorbs heat Q from the principal reservoir and transforms it all into work W . This is, actually, forbidden by the second law of Thermodynamics. The picture just described can only be accepted if work is carried out on the composite system, and the produced heat is returned, not absorbed, by the principal reservoir. This means that Q needs to be negative, i.e. ultimately,

$$\sum_{i=1}^n \frac{Q_i}{T_i} \leq 0 \quad (28)$$

The number of auxiliary Carnot engines can be increased. The temperature of S makes a continuous transition from its initial value to other values, during the cycle, and then back to its initial value. Each Carnot engine was introduced relatively to a temperature value of the system during the cycle. The introduction of more Carnot engines ultimately means a finer sampling of the temperatures range of S during the cycle. We can even think of a limiting process where the number of Carnot engines tends to infinity. In such a case the temperature is sampled continuously, and inequality (28) is transformed in the following one:

$$\oint \frac{\delta Q}{T} \leq 0 \quad (29)$$

Equation (29) is known as *Clausius inequality*. The process through which such an inequality has been derived is quite an artificial one. Yet, the inequality is one of the key points of Thermodynamics, as well soon shall see. The equal sign in (29) occurs, as it can easily be proved, when the process is a reversible one. Consider, then, a reversible process (for example a gas undergoing a cyclical transformation) in which a system goes through an initial state α to a final state ω , and then back to the initial state (see Figure 14). Given that the transformation is reversible, Clausius inequality holds with the equal sign,

$$\oint \frac{\delta Q}{T} = 0$$

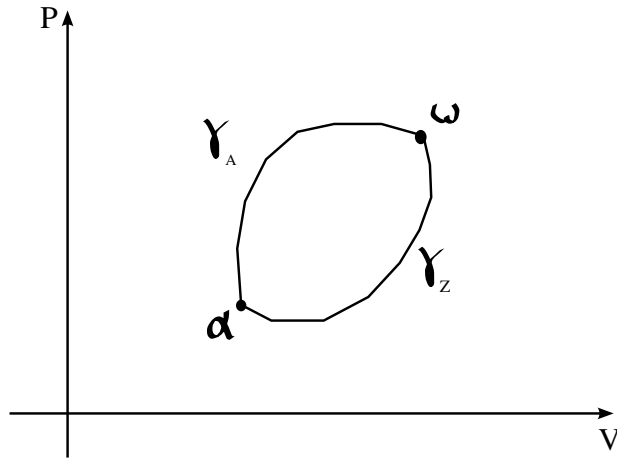


Figure 14: pV diagram of a reversible cycle. The system goes from α to ω , and then back to α , in one cycle. Integral $\int \delta Q/T$ from α to ω is the same for both path γ_A and path γ_Z .

The integral over the closed path can, though, be broken into two integrals over open paths,

$$\oint \frac{\delta Q}{T} = \int_{\alpha}^{\omega} \frac{\delta Q}{T} + \int_{\omega}^{\alpha} \frac{\delta Q}{T} = 0$$

So:

$$\int_{\alpha}^{\omega} \frac{\delta Q}{T} = - \int_{\omega}^{\alpha} \frac{\delta Q}{T}$$

$$\Downarrow$$

$$\int_{\alpha}^{\omega} \frac{\delta Q}{T} = \int_{\alpha}^{\omega} \frac{\delta Q}{T}$$

This last equation shows that each integral is independent on the chosen path. Thus, it can be computed as the difference of a function, which we will indicate as S , between α and ω :

$$\int_{\alpha}^{\omega} \frac{\delta Q}{T} = S_{\omega} - S_{\alpha}$$

In other terms, $\delta Q/T$ is the exact differential of a state function, called *entropy*:

$$\frac{\delta Q}{T} = dS \tag{30}$$

In the above equation the difference in nature between δQ and dS is clear: the second is an exact differential, while the first is not. In fact, the entropy is a state function, while the heat exchanged depends on the specific transformation involved.

Entropy is an important thermodynamic quantity describing the direction in which systems undergo transformations. To see this let us consider an irreversible cycle. This could be formed by an irreversible transformation from α to ω (in this case there is no path connecting the two states as the transformation is irreversible) and a reversible one from ω to α , along a curve γ . Clausius inequality forces us to write:

$$\oint \frac{\delta Q}{T} = \int_{\alpha}^{\omega} \frac{\delta Q}{T} + \int_{\omega}^{\alpha} \frac{\delta Q}{T} \leq 0$$

Now, using the entropy:

$$\int_{\alpha}^{\omega} \frac{\delta Q}{T} + S_{\alpha} - S_{\omega} \leq 0$$

This leads to the following important result:

$$S_{\omega} - S_{\alpha} \geq \int_{\alpha}^{\omega} \frac{\delta Q}{T} \quad (31)$$

What happen if the system considered is isolated? In such a case there is no heat exchange, $\delta Q = 0$, thus:

$$S_{\omega} \geq S_{\alpha}$$

This is a very important conclusion:

for any transformation occurring in an isolated system, the entropy of the final state can never be less than that of the initial state.

For reversible transformations the entropy will, of course, remain unchanged. The stated result provides us with an indicator for any process direction. An isolated system with constant energy can progress through a whole series of transformations compatible with its energy (first law). But, once its state of maximum entropy has been reached, the system will no progress any further. We can say that the state of maximum entropy is the most stable state for an isolated system.

9 Entropy as a function of T and V (and rigorous demonstration of Joule experiment).

In equation (7) the infinitesimal amount of heat was expressed as a function of T and V differentials,

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

Using definition (30) is, therefore, immediate to express the entropy differential as a function of T and V :

$$dS = \frac{1}{T} \frac{\partial U}{\partial T} dT + \frac{1}{T} \left[p + \frac{\partial U}{\partial V} \right] dV \quad (32)$$

where we have dropped the T and V suffixes because we know that S is here considered to depend on these two variables only. Now, dS is an exact differential. From standard Calculus we learn that if an expression like,

$$M(x, y)dx + N(x, y)dy$$

is an exact differential, then the following condition holds:

$$\frac{\partial M}{\partial y} = \frac{\partial N}{\partial x} \quad (33)$$

For dS , which is an exact differential, condition (33) reduces to,

$$\begin{aligned} \frac{\partial}{\partial V} \left(\frac{1}{T} \frac{\partial U}{\partial T} \right) &= \frac{\partial}{\partial T} \left[\frac{1}{T} \left(p + \frac{\partial U}{\partial V} \right) \right] \\ &\Downarrow \\ \frac{1}{T} \frac{\partial^2 U}{\partial V \partial T} &= -\frac{1}{T^2} \left(p + \frac{\partial U}{\partial V} \right) + \frac{1}{T} \frac{\partial p}{\partial T} + \frac{1}{T} \frac{\partial^2 U}{\partial T \partial V} \end{aligned}$$

and eventually, after carrying out few simplifications,

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial p}{\partial T}\right)_V - p \quad (34)$$

where we have re-introduced the T and V suffixes for future clarity. We will now use equation (34) to prove mathematically a result previously introduced and described using an experiment by Joule, the dependency of the internal energy of an ideal gas exclusively on T : $U = U(T)$. For one mole of ideal gas the result $pV = RT$ is valid. Thus, $\partial p/\partial T = R/V$ and equation (34) gives,

$$\left(\frac{\partial U}{\partial V}\right)_T = T \frac{R}{V} - \frac{RT}{V} = 0$$

which means that $U(T, V)$ depends only on T . So, like we said some time ago, this result can be rigorously proved using the second law of Thermodynamics.

10 Calculation of entropy change for irreversible processes

Entropy is calculated as an integral of quantity (30) only for reversible processes. This can be understood by thinking to the way entropy was introduced as a state function. There we had to use Clausius inequality with the equal sign; therefore the infinitesimal amount of heat exchanged, δQ corresponded to a reversible transformation. In other words, when we define dS as $\delta Q/T$, we are allowed to consider infinitesimal heat variations for reversible processes only. What can we do, then, when an entropy change needs to be computed for irreversible transformations? After all this is what normally occurs in nature. We are indeed lucky that entropy is a state function and, as such, depends exclusively on the initial and final states of the transformation, not on the specific transformation is carried out. Irreversible transformations do not possess, for example, a defined curve between two states in a (p, V) diagram, but their entropy variations exist because initial and final states are well defined.

When we are required to compute the entropy variation for an irreversible process, then, we can simply compute $\delta Q/T$ for any reversible process taking the system from the initial to the final state of the irreversible process. Any path from the initial to the final state will produce the same answer, because the integral is independent on the chosen path.

EXAMPLE 6.

1 Kg of water is heated at atmospheric pressure from 20 °C to 100 °C. Knowing that the heat capacity (with constant pressure) of water is $C_p = 4.2 \text{ kJK}^{-1}$, compute water entropy variation.

Solution.

The initial state and the final state are well defined for the system described in this problem. The entropy variation, accordingly, is well defined. In order to compute it, though, we need to find an expression for δQ of a corresponding reversible process, i.e. a transformation taking the water from 20 °C to 100 °C at constant atmospheric pressure. A possibility is, quite obviously, an isobaric process. In this case we have,

$$\delta Q = C_p dT$$

(no work is carried out by the water or on the water), so that,

$$dS = \frac{C_p dT}{T}$$

The entropy variation is given by the integral for the above expression between the absolute temperature $20+273=293$ and the absolute temperature $100+273=373$:

$$\Delta S = \int_{293}^{373} C_p \frac{dT}{T} = C_p [\ln T]_{293}^{373} = C_p \ln \left(\frac{373}{293} \right) = 4.2 \times 10^3 \ln \left(\frac{373}{293} \right)$$

The result is, thus, $\Delta S \approx 1.01 \times 10^3 \text{JK}^{-1}$.

EXAMPLE 7.

An ideal gas undergoes a free expansion, doubling its initial volume. Compute the entropy change for this irreversible process.

Solution.

We have already seen a free expansion while describing Joule experiment. As it was clear from the experiment, the process is irreversible because, once the stopcock is open, the gas diffuses freely in the empty container and there is no way it freely goes back to the first container. We need now to find a reversible process which takes a volume V of gas at temperature T to a new volume $2V$ still at the same temperature, and where no heat exchange has occurred (adiabatic process). The reversible process we will use here is one taking the gas to slowly expand by keeping it in contact with a reservoir at temperature T (isothermal transformation). In such a case, from the first law, δQ is given by:

$$\delta Q = dU + pdV = pdV$$

because $dU = 0$, given that the temperature is kept constant. For the infinitesimal entropy we have:

$$dS = \frac{\delta Q}{T} = \frac{pdV}{T}$$

The quantity whose variation is directly observed in this transformation is the volume. From $pV = nRT$ we express p as a function of T and V , $p = nRT/V$, so that:

$$dS = nR \frac{dV}{V}$$

The total entropy variation is obtained by integrating the above expression between V and $2V$:

$$\Delta S = \int_V^{2V} nR \frac{dV}{V} = nR [\ln V]_V^{2V} = nR \ln 2$$

EXAMPLE 8.

For the system described in EXAMPLE 6, compute the entropy variation for the whole universe.

Solution.

The universe is, in this case, formed by the water and the reservoir that has been used to heat the water from $T_i = 293$ to $T_f = 373$ kelvin degrees. Such reservoir is, thus, at a fixed temperature of $T_f = 373$ K. The heat absorbed by the water has been released by the reservoir. The entropy variation for the reservoir is, thus,

$$\Delta S_{\text{res}} = \frac{-C_p(T_f - T_i)}{T_f}$$

Consequently, the universe entropy is computed as follows:

$$\Delta S_{\text{uni}} = \Delta S_{\text{wat}} + \Delta S_{\text{res}} = C_p \left[\ln \left(\frac{373}{293} \right) - \frac{80}{373} \right] = 0.027 C_p$$

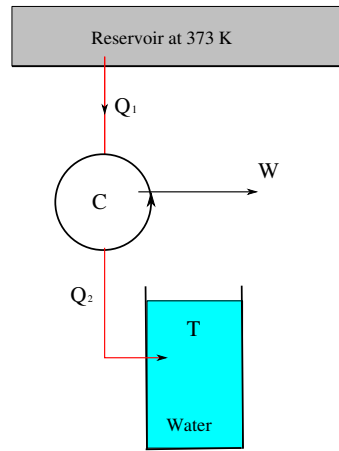


Figure 15: Heating of water using a Carnot engine.

It is, therefore, a positive quantity, as it should be.

It is instructive to calculate the entropy variation for the same experimental set up when the heating is carried out in two steps: first the water temperature is raised from 20 °C to 60 °C and then from 60 °C to 100 °C. As the initial and final states of the process are still the same, the entropy variation for the water is still the same. But now we have two reservoirs, one at 333 K and the other at 373 K. The entropy variation for the two reservoirs is, thus,

$$\Delta S_{\text{resvs}} = - \left(\frac{40}{333} + \frac{40}{373} \right) C_p$$

For the universe we have, this time,

$$\Delta S_{\text{uni}} = \Delta S_{\text{wat}} + \Delta S_{\text{resvs}} = C_p \left[\ln \left(\frac{373}{293} \right) - \frac{40}{333} - \frac{40}{373} \right] = 0.014 C_p$$

It is interesting to observe that the entropy increase is still positive, as it should be, but smaller than with just one reservoir. This is so because two reservoirs, and the related heat transfer in smaller steps, make the process more akin to a quasi-static, reversible process (for which the entropy change is zero).

EXAMPLE 9.

Calculate the universe entropy change for the water heating case (EXAMPLE 6), when heat is supposed to be transferred by a Carnot machine operating between $T_f = 373$ K and $T_i = 293$ K.

Solution.

The experimental set up is shown at Figure 15. If the heat transfer at each cycle is small, we have an engine working in a reversible way. Being the water at constant atmospheric pressure, the heat δQ_2 absorbed by the engine is $C_p dT$. If δQ_1 is the heat released by the reservoir then, thanks to formula (27),

$$\frac{\delta Q_1}{\delta Q_2} = \frac{373}{T} \quad \Rightarrow \quad \delta Q_1 = \frac{373}{T} \delta Q_2$$

The entropy change for water is still the same as in EXAMPLE 6. For the reservoir, though, $\delta Q/T$ is equal to $-\delta Q_1/373$, so that the entropy increase is:

$$\Delta S_{\text{res}} = - \int_{293}^{373} \frac{\delta Q_1}{T} = - \frac{1}{373} \int_{293}^{373} \frac{373}{T} C_p dT = - C_p \int_{293}^{373} \frac{dT}{T} = - C_p \ln \left(\frac{373}{293} \right)$$

For the universe the entropy variation will be:

$$\Delta S_{\text{uni}} = \Delta S_{\text{wat}} + \Delta S_{\text{res}} = C_p \ln \left(\frac{373}{293} \right) - C_p \ln \left(\frac{373}{293} \right) = 0$$

There is no entropy increase as, in this case, the heating is performed reversibly by a Carnot engine.

11 The central equation of Thermodynamics

The first law in infinitesimal form was given in equation (5):

$$dU = \delta Q + \delta W$$

We also know (from equation (6)), that $\delta W = -pdV$ for a reversible mechanical work. For the same reversible process we can, in addition, write $\delta S = \delta Q/T$. Thus, in this case, the first law is written as:

$$dU = TdS - pdV$$

We can extend the previous relation to irreversible processes as well, because it is exclusively formed by state functions. The following relation,

$$TdS = dU + pdV \quad (35)$$

is, thus, known as the *central equation of Thermodynamics* because it encompasses first and second laws of Thermodynamics (containing the entropy), and it is valid for both reversible and irreversible processes.

EXAMPLE 10.

Determine the entropy for a mole of ideal gas.

Solution.

For an ideal gas the internal energy is a function of temperature only, $U = U(T)$, therefore:

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = \frac{dU}{dT}$$

and $dU = C_V dT$. The central equation of Thermodynamics will, accordingly, be written in the following way:

$$TdS = C_V dT + pdV$$

For one mole of ideal gas the equation of state reads, $pV = RT$, from which $p = RT/V$. With this substitution we have:

$$TdS = C_V dT + RT \frac{dV}{V}$$

or,

$$dS = C_V \frac{dT}{T} + R \frac{dV}{V}$$

Integrating this expression we obtain, finally,

$$S = C_V \ln(T) + R \ln(V) + S_0$$

where S_0 is an arbitrary constant (entropy differences are what is measured experimentally).

12 Thermodynamic potentials and Maxwell relations

We have introduced several physical quantities which are generally used in Thermodynamics, like for instance the internal energy U or the entropy S . We could certainly investigate many thermodynamic phenomena just using what we have introduced so far. But as Thermodynamics is a very general science that can be applied to different fields, people have found it convenient to work with additional quantities, like the enthalpy or the free energy. In this section we would like to introduce, explain and work out with what are generally called *thermodynamic potentials*: the enthalpy (H), the free energy (F) and the Gibbs function (G). The internal energy is included among the potentials and we will start from it to find the first of four relations known as *Maxwell relations*.

The central equation of Thermodynamics can be re-written as,

$$dU = TdS - pdV \quad (36)$$

The presence in the above expression of the differentials dS and dV means that U can be thought as a function of S and V : $U = U(S, V)$. We can, therefore, express the differential dU with the general expression:

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

A comparison of this last expression with equation (36) yields:

$$T = \left(\frac{\partial U}{\partial S}\right)_V, \quad p = -\left(\frac{\partial U}{\partial V}\right)_S \quad (37)$$

Also, given that dU is an exact differential, the following condition holds:

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V \quad (38)$$

The above condition is the *first Maxwell relation*. Let us proceed now to the second relation and the concept of enthalpy. *Enthalpy* is a state function defined as:

$$H = U + pV \quad (39)$$

If we differentiate the above expression, obtain:

$$dH = dU + Vdp + pdV$$

But, from (36), $dU + pdV = TdS$. Thus:

$$dH = TdS + Vdp \quad (40)$$

So, now we have a function of the two variables S and p , $H = H(S, p)$. For the differential we would generally write:

$$dH = \left(\frac{\partial H}{\partial S}\right)_p dS + \left(\frac{\partial H}{\partial p}\right)_S dp$$

A comparison of this expression and (40) leads to:

$$T = \left(\frac{\partial H}{\partial S}\right)_p, \quad V = \left(\frac{\partial H}{\partial p}\right)_S \quad (41)$$

Again, given that dH is an exact differential, the following condition, known this time as *second Maxwell relation*, holds:

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p \quad (42)$$

To derive the second Maxwell relation we have essentially acted analogously to what done for deriving the first Maxwell relation. The only difference is that to derive the first relation the accent is set on the internal energy, while for the second relation the enthalpy plays the more decisive role. But: what is enthalpy? Consider a transformation carried out at constant pressure. In this case equation (40) gives $dH = TdS$, because $dp = 0$. In a reversible reaction TdS equals the heat exchanged, δQ . Thus the enthalpy is equivalent to the heat exchanged in a reversible process at constant pressure:

$$dH = \delta Q \quad \text{in an isobaric and reversible process}$$

Let us move on to the next thermodynamic potential, the free energy, known also as Helmholtz function F . This *free energy* is defined as:

$$F = U - TS \quad (43)$$

As done before, let us differentiate expression (43):

$$dF = dU - SdT - TdS$$

From (36) we derive $dU - TdS = -pdV$, therefore the previous expression can be re-written as,

$$dF = -pdV - SdT \quad (44)$$

In the equation just derived F is a function of V and T , $F = F(V, T)$. This means:

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

A comparison of this last form with form (44) for the differential yields:

$$p = -\left(\frac{\partial F}{\partial V}\right)_T, \quad S = -\left(\frac{\partial F}{\partial T}\right)_V \quad (45)$$

Also, given that dF is an exact differential, the following condition holds:

$$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T \quad (46)$$

conditions called the *third Maxwell relation*.

At this point, before proceeding to the last thermodynamic potential, it is appropriate to give some physical meaning to free energy. We can do this by considering the system depicted at Figure 16. This system is in contact with a reservoir at temperature T_0 , from which it absorbs heat Q . System and reservoir are enclosed by a thermally insulated membrane, so that heat exchange with the rest of the universe does not occur, but this membrane is flexible i.e. it can expand and contract. In this way the system can perform work or work can be performed on the system. When the heat Q is absorbed by the system there is, as we know, an entropy change, both for the system and for the reservoir. Given that the system and reservoir are thermally insulated from the rest of the universe, the process is an adiabatic one and, therefore, the entropy change has to be positive or null:

$$\Delta S + \Delta S_0 \geq 0$$

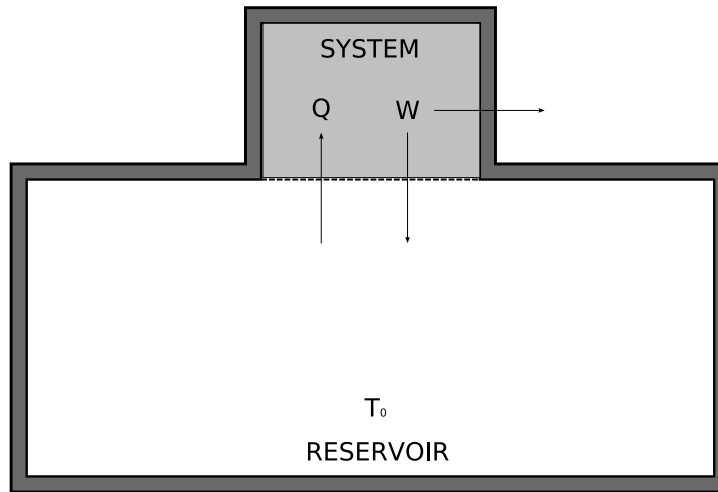


Figure 16: The system and reservoir illustrated in this picture are thermally isolated from the rest of the universe by a membrane. This is not a rigid wall, but flexible enough to allow the system to perform work.

where ΔS and ΔS_0 are the entropy change for the system and reservoir respectively. The reservoir loses heat Q and its temperature is unchanged during the whole process; its entropy change is, thus, $\Delta S_0 = -Q/T_0$. The above expression is consequently turned into the following one:

$$\Delta S - \frac{Q}{T_0} \geq 0$$

or,

$$Q - T_0 \Delta S \leq 0$$

In order to replace Q in the inequality just obtained we can make use of the first law which, for the system here described, reads $\Delta U = Q - W$. Thus $Q = \Delta U + W$ is replaced in the inequality, which is transformed into:

$$\Delta U + W - T_0 \Delta S \leq 0$$

Now, the change in free energy, $U - TS$, for this process is $\Delta F = \Delta U - \Delta(TS) = \Delta U - T_0 \Delta S$, because the temperature of the system at the beginning and the end is T_0 . The inequality can, thus, be re-written as,

$$\Delta(U - TS) + W \leq 0 \quad \Rightarrow \quad \Delta F + W \leq 0$$

We have reached an important conclusion:

$$W \leq -\Delta F, \tag{47}$$

that can be summarized with the following words:

in a process in which the initial and final temperature is the same as the surroundings, the maximum work obtainable is equal to the decrease in free energy

In simpler words we can qualitatively link free energy to available work.

The last potential to be described is the *Gibbs function*. This is defined in the following way:

$$G = H - TS \tag{48}$$

U	$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$
H	$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$
F	$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$
G	$\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T$

Table 1: Maxwell thermodynamic relations.

As we are, by now, use to proceed let us differentiate equation (48):

$$dG = dH - SdT - TdS$$

Now, $dH = d(U + pV) = dU + Vdp + pdV$. Thus:

$$dG = dU + Vdp + pdV - SdT - TdS$$

From equation (36) we have $dU = TdS - pdV$. Replacing this in the above expression we are left with:

$$dG = Vdp - SdT \quad (49)$$

The differential expression (49) assumes $G = G(p, T)$. Through differentiation we, therefore, have:

$$dG = \left(\frac{\partial G}{\partial p}\right)_T dp + \left(\frac{\partial G}{\partial T}\right)_p dT$$

A comparison of this with (49) yields,

$$V = \left(\frac{\partial G}{\partial p}\right)_T, \quad S = -\left(\frac{\partial G}{\partial T}\right)_p \quad (50)$$

Furthermore, the condition for dG to be an exact differential leads to the *fourth Maxwell relation*:

$$\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T \quad (51)$$

The four Maxwell relations have been tabulated together in Table (1) where, in the first column, the thermodynamic potential used to derive them is indicated.

13 A useful relation between ΔF and ΔG

Free energy and Gibbs function are used quite often in practical calculations. In many cases these two quantities are used interchangeably without, in fact, fully justifying the approximation. There is, anyway, an immediate relation between free energy and Gibbs function variations, from which one can make up her mind whether to use one or the other. By definition:

$$F = U - TS$$

while,

$$G = H - TS = U + pV - TS$$

Therefore,

$$G = F + pV$$

Translating this last relation to the finite-difference counterpart we obtain the relation we were looking for:

$$\Delta G = \Delta F + \Delta(pV) \quad (52)$$

From (52) we understand, for instance, that if the variation in pV is small compared to the variation in free energy, then G can easily be approximated by F and vice-versa.

References

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