

The second law of thermodynamics - II

Asaf Pe'er¹

October 11, 2013

1. The second law of thermodynamics for infinitesimal changes

In our discussion so far, we have seen that when considering an isolated system, the second law provides a criterion for the question whether the system changes from state 1 to state 2 or not: **a change occurs if it corresponds to an increase of entropy.**

We would like now to extend the discussion, as well as provide answer to the question of why we chose to define T and P the way we did. For this, we consider now an isolated system which have two equilibrium states which are *infinitely close* together. We are interested in calculating the entropy difference between the two states. As we will shortly see, this will lead us to derive the **fundamental thermodynamic relation**.

Let us assume that state 1 is specified by T, V ; in fact we prefer to work with $\beta (= 1/(k_B T))$, so we specify state 1 by β, V, N . State 2 is specified by $\beta + d\beta, V + dV$, and N : we assume that the number of particles is not changed between the states, hence we omit it from here on. Remember that the system will move from state 1 to state 2 only if the entropy increases in the process.

Recall that the **energy** of a system with a well defined temperature is

$$\bar{E} = \sum_r P(r) E_r, \quad (1)$$

and hence the change in energy when the system moves from state 1 to state 2 is

$$d\bar{E} = \sum_r P(r) dE_r + \sum_r E_r dP(r) \quad (2)$$

In fact, as we have seen that the fluctuations in the energy are of the order $N^{-1/2}$, we don't need the averaging, and we can write $E = \bar{E}$, as we will do from here on.

Recall the calculation of $P(r)$ (the second law of thermodynamics - part I, eq. 35),

$$P(r) = \frac{1}{Z} e^{-\beta E_r}, \quad (3)$$

¹Physics Dep., University College Cork

where

$$Z \equiv \sum_r e^{-\beta E_r}, \quad (4)$$

from which we can write

$$\ln P(r) = -\beta E_r - \ln Z, \quad \rightarrow \quad E_r = -\frac{1}{\beta} (\ln Z + \ln P(r)) \quad (5)$$

We can now write the second term in Equation 2 as

$$\sum_r E_r dP(r) = -\frac{1}{\beta} \ln Z \sum_r dP(r) - \frac{1}{\beta} \sum_r \ln(P(r)) dP(r) \quad (6)$$

Since the total probability is unity, $\sum_r dP(r) = 0$, and only the 2nd term in Equation 6 remains,

$$\sum_r E_r dP(r) = -\frac{1}{\beta} \sum_r \ln(P(r)) dP(r) \quad (7)$$

Recall the definition of the entropy,

$$S = -k_B \sum_r P(r) \ln P(r), \quad (8)$$

from which it follows that

$$dS = -k_B \left(\sum_r \ln P(r) dP(r) + \sum_r P(r) \frac{dP(r)}{P(r)} \right) = -k_B \sum_r \ln P(r) dP(r) \quad (9)$$

where again we have used $\sum_r dP(r) = 0$. Comparing Equations 7 and 9, we get

$$\sum_r E_r dP(r) = \frac{1}{\beta k_B} dS = T dS \quad (10)$$

Remember that Equation 10 is the second term in Equation 2. We thus conclude, that the 2nd term in Equation 2, representing part of the energy change dE when the system is going from state 1 to state 2 due to a change in the probabilities of the system to be in the different energy levels E_1, E_2, \dots is related to the **change in entropy of the system**.

Let us now look at the first term in Equation 2:

$$\sum_r P(r) dE_r = \sum_r P(r) \frac{dE_r}{dV} dV \quad (11)$$

Equation 11 requires a short explanation: the energy levels E_r do **not** depend on the temperature. They depend only on the microscopic structure of the system, which in turn depend

on the external parameters. For example, when discussing paramagnet, the energy levels depend on the strength of the magnetic field. In the current context, these energy levels depend only on the volume.

If a system is at a state r , and it remains at state r *at all times*, then a change in the volume from V to $V + dV$ produces an energy change:

$$dE_r = \frac{dE_r}{dV} dV \equiv -p_r dV, \quad (12)$$

where p_r is defined to be the pressure of the system at state r . Thus dE_r is the work done on the system in state r to produce the volume change.

If we don't know that the system is in state r , but we only know the probability of the system to be in state r , $P(R)$, the pressure p is then the average,

$$p = \sum_r P(r) \left(-\frac{dE_r}{dV} \right), \quad (13)$$

in which case Equation 11 becomes

$$\sum_r P(r) dE_r = -p dV \quad (14)$$

Before wrapping up, we should notice a delicate point: by the definition of pressure as $p_r = dE_r/dV$, we have assumed that the sole effect of changing the volume is changing the energy levels. This is not necessarily the case, as transitions between different energy levels may occur. However, by keeping the rate of change of the volume very slow, such transitions are prevented. Thus, we require a **quasistatic change**. But recall, that this was our requirement when we defined thermodynamic pressure at the beginning !.

Combined together, Equations 2, 10 and 14 we obtain the **fundamental thermodynamic relation**

$$\boxed{dE = TdS - pdV} \quad (15)$$

which is generally valid for neighboring states, infinitesimally close to each other.

Equation 15 can be compared to the first law of thermodynamics, $dE = dQ + dW$; identifying dW with $(-pdV)$ leads to the identification of dQ with TdS . This is correct, though, **for infinitesimal reversible changes only**.

Thus, the equation $dS = \frac{dQ}{T}$ implies that if we supply an infinitesimal amount of heat dQ to a system *reversibly* at temperature T , the entropy of the system increases by dQ/T .

If the infinitesimal change is *irreversible*, then we have, in general

$$\begin{aligned} dW &\geq -pdV; \\ dS &\geq \frac{dQ}{T}. \end{aligned} \tag{16}$$

Example. Consider the free (adiabatic) expansion of a gas into a vacuum (“the piston breaks”). The system as a whole is isolated, and thus $dQ = 0$. The expansion occurs into vacuum, and so no work is done in an infinitesimal change of the volume and $dW = 0$. Thus, $dE = 0$.

The process is irreversible, and so we expect $dW > -pdV$. Does this make sense ?

$$\begin{aligned} 0 &= TdS - pdV \\ TdS &= pdV \\ dV &> 0 \rightarrow dS > 0. \end{aligned} \tag{17}$$

Thus, the entropy increases in this process.

2. Maxwell’s thermodynamic relations

Let us have a look again at the fundamental relation, Equation 15, $dE = TdS - pdV$. This implies that if $dS = 0$, then $dE = -pdV$, or alternatively

$$p = - \left(\frac{\partial E}{\partial V} \right)_{S=const} \tag{18}$$

Similarly, if $dV = 0$, then $dE = TdS$, or

$$T = \left(\frac{\partial E}{\partial S} \right)_{V=const} \tag{19}$$

(recall that this is just the entropy based definition of the temperature). We can now use

$$\frac{\partial^2 E}{\partial S \partial V} = \frac{\partial^2 E}{\partial V \partial S} \tag{20}$$

to write

$$\begin{aligned} \frac{\partial}{\partial S} \left[\left(\frac{\partial E}{\partial V} \right)_S \right]_V &= - \left(\frac{\partial p}{\partial S} \right)_{V=const} \\ \frac{\partial}{\partial V} \left[\left(\frac{\partial E}{\partial S} \right)_V \right]_S &= \left(\frac{\partial T}{\partial V} \right)_{S=const} \end{aligned} \tag{21}$$

From which we get

$$\left(\frac{\partial T}{\partial V} \right)_{S=const} = - \left(\frac{\partial p}{\partial S} \right)_{V=const}. \tag{22}$$

This is the first of **four Maxwell’s relations**, which are very useful in relating different thermodynamic quantities to each other. These equations hold for *any* thermodynamic system in equilibrium, which make them so powerful.

The other 3 Maxwell’s equation follow from the definition of the Helmholtz and Gibbs functions as well as the enthalpy, and are

$$\begin{aligned} \left(\frac{\partial S}{\partial V}\right)_{T=const} &= \left(\frac{\partial p}{\partial T}\right)_{V=const} \\ \left(\frac{\partial S}{\partial p}\right)_{T=const} &= -\left(\frac{\partial V}{\partial T}\right)_{p=const} \\ \left(\frac{\partial T}{\partial p}\right)_{S=const} &= \left(\frac{\partial V}{\partial S}\right)_{p=const} \end{aligned} \tag{23}$$

3. Generalization of the second law to non-isolated systems: the Clausius inequality

We have shown that for *isolated systems*, a natural change from state 1 to state 2 is accompanied by an entropy increase:

$$\Delta S = S_2 - S_1 > 0. \tag{24}$$

In the (theoretical) limit of a reversible process, the system can change back from state 2 to state 1, and thus $\Delta S = 0$. Combined, we got

$$\Delta S \geq 0 \tag{25}$$

where the “=” sign holds for reversible processes only.

Consider now a system that is kept at constant temperature T_0 and pressure, p_0 . You can think of a system coupled *both* thermally and mechanically to a heat bath. The composed (system + heat bath) are isolated from the rest of the world. The system is separated from the heat bath by a membrane that allow heat transfer, and can also move.

As the system changes from state 1 to state 2, the total (system + heat bath) entropy, $S_{tot} = S + S_0$ must increase,

$$\Delta S_{tot} = \Delta S + \Delta S_0 \geq 0 \tag{26}$$

(S is the entropy of the system, and S_0 is the entropy of the heat bath).

Let us assume that in the process, an amount of heat Q was transferred from the heat bath to the system. The heat bath is big, and so its temperature T_0 and pressure p_0 are not changed. Hence, from the point of view of the heat bath, the change is reversible, and

$$\Delta S_0 = -\frac{Q}{T_0}, \tag{27}$$

and Equation 26 becomes

$$\Delta S - \frac{Q}{T_0} \geq 0. \quad (28)$$

We can write down the first law, $\Delta E = Q + W$ where ΔE is the change in energy of the system and W is the work done on it by the heat bath, $W = -P_0\Delta V$ as

$$Q = \Delta E + p_0\Delta V. \quad (29)$$

Combined with Equation 28, we get

$$\Delta S - \frac{\Delta E + p_0\Delta V}{T_0} \geq 0. \quad (30)$$

Equation 30 is thus the extension of the principle of entropy increase to a system which is surrounding at constant temperature T_0 and constant pressure p_0 . It is known as *Clausius's inequality*. It states a criterion for the direction of natural processes and for equilibrium.

–10–

4. The Helmholtz free energy

Recall that the Helmholtz free energy was defined by

$$\boxed{F = E - TS} \quad (31)$$

and is very useful for systems having constant volume in equilibrium, in contact with a heat bath. In a process in which the system changes its state, the Helmholtz free energy changes according to

$$\Delta F = \Delta E - T\Delta S - S\Delta T. \quad (32)$$

If the process is isothermal, namely the temperature is held constant and equal to T_0 , then

$$\Delta F = \Delta E - T_0\Delta S \quad (33)$$

Recalling that the volume is assumed constant, the generalized version of the second law (Equation 30) becomes

$$\Delta F \leq 0. \quad (34)$$

This is true for processes for which $T_1 = T_2$ and $V_1 = V_2$; note, though, that *during* the process the temperature and the volume may change.

Further note that for processes for which the volume can (infinitesimally) change, we can use Equation 15 in Equation 32 to write $\Delta F = -S\Delta T - p\Delta V$. Differentiating this equation

leads to the second of Maxwell's relation introduced in §2, Equation 23: $S = -(\partial F/\partial T)_V$, $p = -(\partial F/\partial V)_T$, and cross-differentiation gives

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

5. Gibbs free energy

If a system is in contact with a heat bath **at constant temperature and constant pressure**, the easiest way to describe the state of the system is using **Gibbs free energy**, defined by

$$G \equiv E + pV - TS \quad (35)$$

The Gibbs free energy is a function of state. When the state of the system changes, the Gibbs free energy change,

$$\Delta G = \Delta E + p\Delta V + V\Delta p - T\Delta S - S\Delta T, \quad (36)$$

and if $T = T_0$, $p = p_0$ are held constant, we have

$$\Delta G = \Delta E + p_0\Delta V - T_0\Delta S. \quad (37)$$

The generalized second law (Equation 30) becomes in this case

$$\Delta G \leq 0. \quad (38)$$

Using again the fundamental thermodynamic relation (Equation 15), we can write $\Delta G = -S\Delta T + V\Delta p$, from which the 3rd of the Maxwell's relation (Equation 23) follows: $S = -(\partial G/\partial T)_p$, $V = (\partial G/\partial p)_T$, and by cross differentiation,

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

6. Enthalpy

Lastly, we consider a thermally isolated system held at constant pressure p . As the system is isolated, $\Delta Q = 0$, or $\Delta E = -p\Delta V$. Such a system is best described by the **enthalpy**, defined by

$$H \equiv E + pV. \quad (39)$$

During a change in the state of the system,

$$\Delta H = \Delta E + p\Delta V + V\Delta p = \Delta E + p\Delta V \quad (40)$$

The condition of constant enthalpy, $\Delta H = 0$ replaces that of constant energy in a totally isolated system. In a spontaneous process, the entropy increases, and the enthalpy remains constant.

Using again the fundamental thermodynamic relation (Equation 15), we can write $\Delta H = T\Delta S + V\Delta p$, from which the 4th of the Maxwell's relation (Equation 23) follows. $T = (\partial H/\partial S)_p$, $V = (\partial H/\partial p)_S$, and by cross differentiation,

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

We can summarize the findings in the following table:

System	
1. Initial and final T , p equal:	$\Delta G = \Delta E + p_0\Delta V - T_0\Delta S \leq 0$
2. Initial and final T , V equal:	$\Delta F = \Delta E - T_0\Delta S \leq 0$
3. Thermally isolated, constant pressure:	$\Delta H = \Delta E + p_0\Delta V = 0$; $\Delta S \geq 0$
4. Totally isolated system:	$\Delta E = 0$; $\Delta S \geq 0$

7. Using Maxwell's relations in solving problems

The four Maxwell's relations derived from the 4 thermodynamic quantities, E , F , G and H are

$$\begin{array}{l} \left(\frac{\partial T}{\partial V}\right)_{S=const} = - \left(\frac{\partial p}{\partial S}\right)_{V=const} \\ \left(\frac{\partial S}{\partial V}\right)_{T=const} = \left(\frac{\partial p}{\partial T}\right)_{V=const} \\ \left(\frac{\partial S}{\partial p}\right)_{T=const} = - \left(\frac{\partial V}{\partial T}\right)_{p=const} \\ \left(\frac{\partial T}{\partial p}\right)_{S=const} = \left(\frac{\partial V}{\partial S}\right)_{p=const} \end{array} \quad (41)$$

Let us see how we can use Maxwell's relation to solve problems in thermodynamic. For example, let us look at the heat capacities, and find expressions for $(\partial C_p/\partial p)_T$ and $(\partial C_V/\partial p)_T$ as a function of the thermodynamic variables T , V and p .

This is done as follows: from the definitions of C_p and C_V ,

$$\begin{array}{l} C_V = \left(\frac{\partial Q}{\partial T}\right)_V = T \left(\frac{\partial S}{\partial T}\right)_V \\ C_p = \left(\frac{\partial Q}{\partial T}\right)_p = T \left(\frac{\partial S}{\partial T}\right)_p \end{array} \quad (42)$$

Thus,

$$\begin{aligned} \left(\frac{\partial C_p}{\partial p}\right)_T &= \left(\frac{\partial}{\partial p} T \left(\frac{\partial S}{\partial T}\right)_p\right)_T \\ &= T \left(\frac{\partial}{\partial p} \left(\frac{\partial S}{\partial T}\right)_p\right)_T \\ &= T \left(\frac{\partial}{\partial T} \left(\frac{\partial S}{\partial p}\right)_T\right)_p \end{aligned} \quad (43)$$

where in the last line we used the fact that the order of differentiation doesn't matter. Using now the 3rd Maxwell's relation, $(\partial S/\partial p)_T = -(\partial V/\partial T)_p$, we can write

$$\left(\frac{\partial C_p}{\partial p}\right)_T = -T \left(\frac{\partial}{\partial T} \left(\frac{\partial V}{\partial T}\right)_p\right)_p = -T \left(\frac{\partial^2 V}{\partial T^2}\right)_p. \quad (44)$$

For an ideal gas, $V = nRT/p$, and thus

$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{nR}{p} \propto T^0, \quad \rightarrow \quad \left(\frac{\partial C_p}{\partial p}\right)_T = 0. \quad (45)$$

A similar calculation for C_V yields

$$\begin{aligned} \left(\frac{\partial C_V}{\partial V}\right)_T &= \left(\frac{\partial}{\partial V} T \left(\frac{\partial S}{\partial T}\right)_V\right)_T \\ &= T \left(\frac{\partial}{\partial V} \left(\frac{\partial S}{\partial T}\right)_V\right)_T \\ &= T \left(\frac{\partial}{\partial T} \left(\frac{\partial S}{\partial V}\right)_T\right)_V. \end{aligned} \quad (46)$$

Using the 2nd Maxwell's relation, $(\partial S/\partial V)_T = (\partial p/\partial T)_V$ we can write this as

$$\left(\frac{\partial C_V}{\partial V}\right)_T = T \left(\frac{\partial}{\partial T} \left(\frac{\partial p}{\partial T}\right)_V\right)_V = T \left(\frac{\partial^2 p}{\partial T^2}\right)_V. \quad (47)$$

Again we find that for an ideal gas, $(\partial C_V/\partial V)_T = 0$.

8. Applications: entropy change in an arbitrary process

The most important thing to remember is that **entropy is a function of state**. Thus, the difference in entropy between states 1 and 2 of a system depends only on these states. If a system changes from state 1 to 2 via different processes, the change in entropy of the system is always the same; but the entropy of the *environment* may differ. A *reversible* process is distinguished by the fact that the change in entropy of the environment exactly cancels the change of entropy of the system, so that the **total entropy is conserved**. For a reversible process, since $dQ = TdS$, the change in entropy is

$$\Delta S = S_2 - S_1 = \int_1^2 \frac{dQ}{T} \quad (48)$$

(note that the integral must be taken along a *reversible path* connecting the two states).

Example. What is the entropy change in a free (adiabatic) expansion of an ideal gas into a vacuum? In this process, there is no heat flow and so $\Delta Q = 0$. No work is done - $\Delta W = 0$. Thus, $\Delta E = 0$. By definition of ideal gas, the energy is a function of the temperature only, $E = E(T)$, and thus in the process $\Delta T = 0$. The entropy, though, clearly increases in the process.

Clearly, the process is *irreversible*. Thus, our problem is to identify a reversible path between the initial and final states. The solution is to calculate the entropy difference using some reversible process. Since the entropy is a function of state, the entropy difference must be the same. Let us demonstrate this.

Consider, first, **isothermal expansion** from (p_1, V_1) to (p_2, V_2) . The entropy change in this process is

$$\Delta S = \int_1^2 \frac{dQ}{T_1} = \frac{\Delta Q_{iso}}{T_1}. \quad (49)$$

We can calculate ΔQ_{iso} using the first law of thermodynamics, $\Delta E = \Delta Q_{iso} + W_{iso} = 0$, where $\Delta E = 0$ due to the fact that the temperature is held constant in an isothermal process. Thus, $\Delta Q_{iso} = -\Delta W$, the mechanical work. We can now use

$$\Delta W = - \int_1^2 p dV = - \int_1^2 \frac{nRT_1 dV}{V} = -nRT_1 \ln \left(\frac{V_2}{V_1} \right). \quad (50)$$

We thus get

$$\Delta S = nR \ln \left(\frac{V_2}{V_1} \right). \quad (51)$$

As argued, this should be the entropy change of the system when it undergoes free adiabatic expansion rather than reversible isothermal expansion.

Now, let us repeat the entropy calculation, but instead of taking isothermal expansion we will take a different path: for example, we assume that the system undergoes **isobaric** expansion (=expansion at constant pressure) from volume V_1 to volume V_2 , which is followed by cooling of the gas at constant volume. This is demonstrated in Figure 1. We expect to find the same entropy difference. Let us see:

The entropy change during the isobaric expansion is

$$\Delta S_1 = \int_1^3 \frac{dQ}{T} = \int_1^3 \frac{C_P dT}{T} = C_P \ln \left(\frac{T_3}{T_1} \right) \quad (52)$$

Using the ideal gas law, $pV = nRT$, we get $V_3/V_1 = T_3/T_1$ ($p_3 = p_1$ in isobaric expansion).

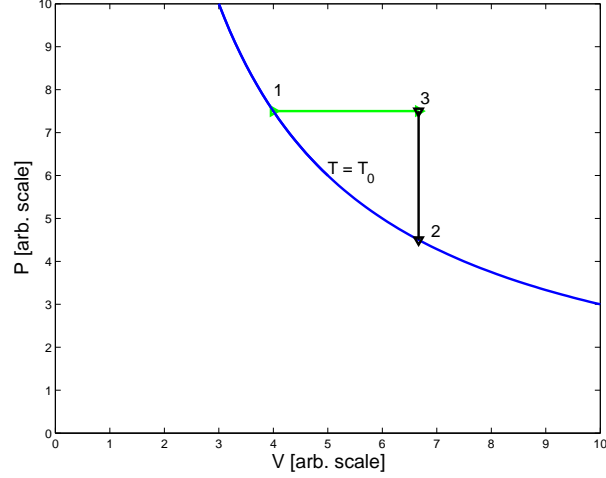


Fig. 1.— A pV diagram. Getting to point 2 from point 1 can be done by isothermal expansion (blue curve) or by isobaric expansion to point 3 (green line) followed by cooling (=pressure drop) at constant volume (black line). Both ways reveal the same entropy difference, as the entropy is a *function of state*.

Using $V_3 = V_2$ we get

$$\Delta S_1 = C_p \ln \left(\frac{V_2}{V_1} \right). \quad (53)$$

At a second step, we need to cool the gas keeping the volume constant. The entropy change in this process is

$$\Delta S_2 = \int_3^2 \frac{dQ}{T} = \int_3^2 \frac{C_V dT}{T} = -C_V \ln \left(\frac{T_3}{T_2} \right) \quad (54)$$

Using again the ideal gas law, we get $T_3/T_2 = p_3/p_2$, and

$$\Delta S_2 = -C_V \ln \left(\frac{p_3}{p_2} \right) = -C_V \ln \left(\frac{p_1}{p_2} \right) \quad (55)$$

where the last equality holds since $p_3 = p_1$ in isobaric expansion. Using the ideal gas law once again and recalling that in the first path we took (isothermal expansion), $T_2 = T_1$, we find $p_1/p_2 = V_2/V_1$. The total entropy change is thus

$$\begin{aligned} \Delta S = \Delta S_1 + \Delta S_2 &= C_P \ln \left(\frac{V_2}{V_1} \right) - C_V \ln \left(\frac{V_2}{V_1} \right) \\ &= (C_P - C_V) \ln \left(\frac{V_2}{V_1} \right) = nR \ln \left(\frac{V_2}{V_1} \right) \end{aligned} \quad (56)$$

which is identical to the result in Equation 51. Thus, as claimed, the entropy change does not depend on the path taken.

9. The third law of thermodynamics

The treatment above gives the *difference* in entropy between different states (e.g., Equation 56). The third law of thermodynamics aims at giving an *absolute* value for the entropy. It deals with the entropy of a system as its the temperature approaches zero. As such, its usefulness is more limited than that of the first and second laws.

Consider a system having energy levels $E_1 < E_2 < \dots < E_r < \dots$. Recall that the probability of a system to be in a state E_r is

$$P(E_r) = \frac{1}{Z} g(E_r) e^{-\beta E_r},$$

where $g(E_r)$ is the degeneracy of E_r .

If the temperature is so low that $E_2 - E_1 \gg k_B T$, then $P(E_1) \gg P(E_2)$, and even more so for E_3, E_4, \dots . Thus, in this situation

$$P(E_1) \approx 1; \quad P(E_r) \approx 0 \quad (r > 1). \quad (57)$$

(“There is not enough thermal energy $k_B T$ to put the system in higher energy level than the minimum one”). From the definition of the entropy,

$$S = k_B \ln \Omega = k_B \ln g_1. \quad (58)$$

(This can be seen as $P(r) = 1/g_r$ and $S = -k_B \sum_r P(r) \ln P(r)$).

If the ground state is *non-degenerated* (was not proved theoretically, but seen experimentally), then

$$\lim_{T \rightarrow 0} S = k_B \ln 1 = 0. \quad (59)$$

Equation 59 is known as **the third law of thermodynamics**.

9.1. Consequences - 1: zero heat capacities at $T = 0$

We have seen (e.g., Equations 48, 51) that when the temperature changes (e.g., in constant pressure), the entropy changes

$$S(T_2) - S(T_1) = \int_1^2 \frac{dQ}{T} = \int_1^2 \frac{C_p dT}{T} = C_p \ln \frac{T_2}{T_1}. \quad (60)$$

If we take the limit $T_1 \rightarrow 0$, then $S(T_1) \rightarrow 0$, and $\ln(T_2/T_1) \rightarrow \infty$. Thus, to keep $S(T_2)$ finite, we must have

$$C_p \rightarrow 0 \quad \text{as} \quad T \rightarrow 0 \quad (61)$$

Thus, the third law of thermodynamics predicts that the heat capacities (same argument holds for C_V) must tend to zero as $T \rightarrow 0$. This was validated experimentally by Nernst et. al. (1910 - 1912).

This fact also implies that no gas can remain ideal when $T \rightarrow 0$. Ideal gas obeys the equation of state, $pV = nRT$, where $R = C_p - C_V$. But when $T \rightarrow 0$, both C_p and $C_V \rightarrow 0$, hence $R \rightarrow 0$ and the equation of state for ideal gases no longer holds. Physically, this is because the distance between the molecules can no longer be considered much larger than the size of the gas molecules.

9.2. Consequences - 2: entropies of systems in different states

At $T = 292^\circ$ K, two forms of tin coexist in equilibrium: grey (insulator) and white (metal). In order to transform one mole of grey tin into white, latent heat L is needed. While at 292° K the transition can be rapid, at lower temperatures it is much slower. Thus, if one cools white tin, it continues to exist. The entropies of white and grey tins at temperatures T_0 can be written as

$$\begin{aligned} S_{\text{White}}(T_0) &= S_{\text{White}}(0) + \int_0^{T_0} C_{\text{White}}(T) \frac{dT}{T} \\ S_{\text{Grey}}(T_0) &= S_{\text{Grey}}(0) + \int_0^{T_0} C_{\text{Grey}}(T) \frac{dT}{T}. \end{aligned} \quad (62)$$

The third law tells us that $S_{\text{White}}(0) = S_{\text{Grey}}(0) = 0$, and therefore

$$S_{\text{White}}(T_0) - S_{\text{Grey}}(T_0) = \int_0^{T_0} [C_{\text{White}}(T) - C_{\text{Grey}}(T)] \frac{dT}{T} \quad (63)$$

To convert one mole of grey tin into white tin at temperature T_0 one must supply a quantity of heat L at this temperature, and so the entropy increases by L/T_0 ,

$$S_{\text{White}}(T_0) - S_{\text{Grey}}(T_0) = \frac{L}{T_0}. \quad (64)$$

Thus,

$$\frac{L}{T_0} = \int_0^{T_0} [C_{\text{White}}(T) - C_{\text{Grey}}(T)] \frac{dT}{T} \quad (65)$$

Both sides of Equation 65 were measured experimentally (and found in good agreement, of course).

10. Absolute entropy of an ideal gas

An ideal gas obeys the equation of state $pV = Nk_B T$. In addition, in an ideal gas the internal energy depends only on the temperature, and thus

$$dE = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV = \left(\frac{\partial E}{\partial T}\right)_V dT. \quad (66)$$

From the definition of the heat capacity (per molecule) we get $(\partial E/\partial T)_V = Nc_V$, where N is the total number of molecules in volume V . Thus, $dE = Nc_V dT$.

We can now use the fundamental relation $dE = TdS - pdV$ and the ideal gas equation of state to write

$$Nc_V dT = TdS - \frac{Nk_B T}{V} dV, \quad (67)$$

or

$$dS = \frac{Nc_V}{T} dT + \frac{Nk_B}{V} dV. \quad (68)$$

This expression can be integrated to give

$$S = Nc_v \int \frac{dT}{T} + Nk_B \int \frac{dV}{V} = Nc_v \ln T + Nk_B \ln V + C' \quad (69)$$

where C' is a constant of integration. (Note of course that equation 69 cannot be correct in the limit $T \rightarrow 0$, since $c_V \rightarrow 0$ as discussed above, while we took it out of the integration.)

We know that entropy is an *extensive* quantity, thus it is linearly proportional to N . However, both the second term ($\propto N \ln V$) and the third term (C') seem to violate this (as the system doubles, both N and V double).

In order to make the entropy extensive, the solution is that C' (that does not depend on V or T) has the form

$$C' = -Nk_B \ln N + NC, \quad (70)$$

where C is constant that does not depend on N . The entropy in this case is

$$S = Nc_v \ln T + Nk_B \ln \frac{V}{N} + NC, \quad (71)$$

which is manifestly an extensive quantity.

10.1. Example: mixing of two ideal gases

Consider two ideal gases having the same temperature T and same pressure p , initially separated (V_1, N_1 and V_2, N_2) that are being mixed. This process is clearly irreversible:

the two gases will not separate again spontaneously. How does the entropy change in the process ?

The entropy is additive, and thus before the mixing

$$S_i = S_1 + S_2 = N_1 \left(c_v \ln T + k_B \ln \frac{V_1}{N_1} \right) + N_1 C_1 + N_2 \left(c_v \ln T + k_B \ln \frac{V_2}{N_2} \right) + N_2 C_2. \quad (72)$$

After the mixing, each gas occupies the entire volume, and thus

$$S_f = N_1 \left(c_v \ln T + k_B \ln \frac{V}{N_1} \right) + N_1 C_1 + N_2 \left(c_v \ln T + k_B \ln \frac{V}{N_2} \right) + N_2 C_2 \quad (73)$$

We thus find that

$$\Delta S = S_f - S_i = N_1 k_B \ln \frac{V}{V_1} + N_2 k_B \ln \frac{V}{V_2}, \quad (74)$$

which is always positive - as we would expect. And a final question: how would the answer change if it was the same gas in either side of the initial partition ?