

# Fundamentals of Thermodynamics, Part 1

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### **Acknowledgements**

I would like to thank Annabel Azziz for the typing of this work, and Professor Marcelo Ubriaco for his continuous encouragement.

The second part of this work will discuss further on stochastic problems as an approach to the many-body problem.

# Contents

<b>1</b>	<b>Thermodynamic Quantities</b>	<b>1</b>
<b>2</b>	<b>Types of Thermodynamic Processes</b>	<b>2</b>
<b>3</b>	<b>The First Law of Thermodynamics</b>	<b>3</b>
<b>4</b>	<b>The Second Law of Thermodynamics</b>	<b>7</b>
<b>5</b>	<b>The Third Law of Thermodynamics</b>	<b>9</b>
<b>6</b>	<b>The Carn. Cyc. and the <math>2^{nd}</math> and <math>3^{rd}</math> Laws</b>	<b>10</b>
<b>7</b>	<b>Enthalpy, <math>H</math></b>	<b>14</b>
7.1	Enthalpy Eqs. and Their Maxwell Rel. . . . .	20
<b>8</b>	<b>Helm. Free Energy in Classical Therm.</b>	<b>21</b>
8.1	Helm. Free Energy and Its Maxwell Rel. . . . .	22
<b>9</b>	<b>Gibbs Free Energy in Classical Therm.</b>	<b>23</b>
9.1	Gibbs Free Energy and Its Maxwell Relationship . . . . .	24
9.2	Example of Gibbs Free Energy . . . . .	24
<b>10</b>	<b>Brief Summary of Quantum Mechanics</b>	<b>26</b>
<b>11</b>	<b>Enclosed Systems in Equilibrium</b>	<b>29</b>
11.1	Probability of finding the system at certain classic or quantum states . . . . .	29
11.2	Canonical Ensembles . . . . .	30
<b>12</b>	<b>Deriv. of the Helmholtz Free Energy</b>	<b>32</b>
12.1	Entropy From a Statistical Point of View . . . . .	34
12.2	Examples of the Helmholtz Free Energy . . . . .	34
12.3	Change of the Part. Funct. and Free Energy . . . . .	38

<b>13 Stoch. Appr. to Many-Body Problems</b>	<b>40</b>
13.1 Solution of the Langevin Equation . . . . .	41
13.2 Average Kinetic Energy in Brownian Motion . . . . .	42
13.3 The Liouville Equation . . . . .	44
13.4 The Fokker-Planck Equation . . . . .	46

# Chapter 1

## Thermodynamic Quantities

1.  $P$  = pressure of the system against the surroundings
2.  $U$  = internal energy of the system
3.  $Q$  = heat flow into the system
4.  $W$  = work delivery by the system
5.  $T$  = absolute temperature (sometimes called  $\theta$ )
6.  $F$  = Helmholtz free energy (sometimes called  $A$ )
7.  $G$  = Gibbs free energy (sometimes called  $F$ )
8.  $S$  = entropy
9.  $H$  = enthalpy
10.  $\xi_i$  = pseudothermodynamic potentials associated with the element of the system of the mass  $m_i$
11.  $V$  = volume of the system

# Chapter 2

## Types of Thermodynamic Processes

1. *Adiabatic*: the energy may change without exchange of heat or matter with the environment, only work
2. *Diathermal*: allows transfer of heat but not matter
3. *Semipermeable partition*: allows transfer heat and some matter
4. *Permeable partition*: allows transfer of both heat and matter
5. *Quasistatic process*: the process develops infinitely slowly and goes from one equilibrium to the next—it is interpreted as a reversible process

# Chapter 3

## The First Law of Thermodynamics

The First Law expresses the conservation of energy concerning the three quantities  $U$ ,  $Q$ ,  $W$ , and  $n_i$  (the number of elements of type  $i$  with potential  $u_i$ ):

$$U = Q - W + \mu_i n_i .$$

Thus, the variation of the internal energy of the system  $dU$  is equal to the amount of heat supplied to the system  $dQ$  minus the energy delivered by the system in the form of work,  $dW$ , plus the contribution of the chemical potential per unit mass of the elements of the system  $n_i$ :

$$dU = dQ - dW + \mu_i dn_i .$$

The last term was introduced by Gibbs; it is another extensive property that we will later discuss in the relation to other properties of the system. We will also see its relevance to open systems.

Thus, from state 1 to state 2

$$U_2 - U_1 = \int_1^2 dQ - \int_1^2 dW .$$

The internal energy  $U$  is a point function of the system and depends on the parameters that define the state (for example, pressure and temperature). For  $Q$  and  $W$  in the previous equation, we left the integration signs because they may depend (for instance, in a non-reversible process) on the path that takes the state from 1 to 2. In other words,  $Q$  and  $W$  are not, in those cases, perfectly differentiable functions.

At this point, we will try to offer some mathematical reasoning to clarify these statements.

Assume a function  $F$  of two variables  $x$  and  $y$ ,  $F = F(x, y)$ , which has an exact differentiability such that

$$dF = \left(\frac{\partial F}{\partial x}\right)dx + \left(\frac{\partial F}{\partial y}\right)dy .$$

Geometrically,  $F$  represents a surface in the  $x, y, z$  space.

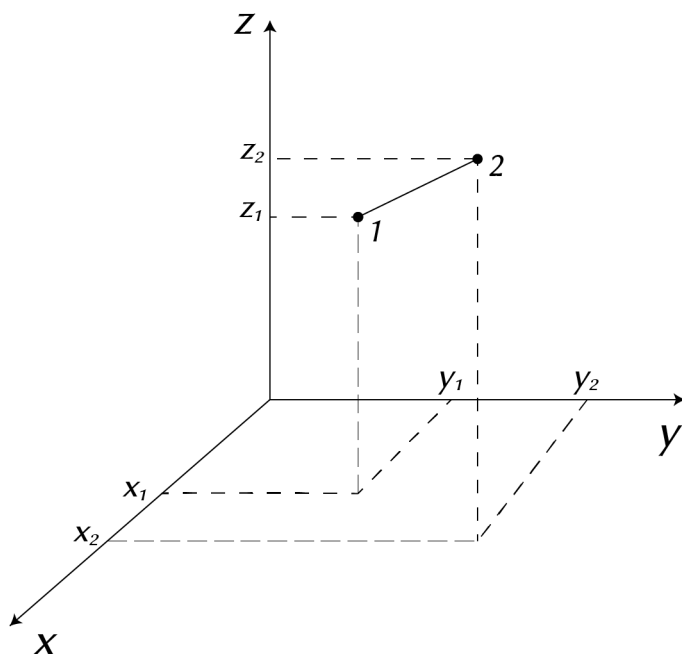


In this case, we may go from 1 to 2 on a unique curve and come back on the same one. However, if  $F(x, y)$  is such that

$$dF = A(x, y)dx + B(x, y)dy$$

and  $A$  and  $B$  are not the partial derivatives of  $F$  with respect to  $x$  and  $y$ , respectively, then  $F(1) - F(2)$  will in general depend on the path that goes from 1 to 2. Thus,

$$[F(2) - F(1)]_{C_1} \neq [F(2) - F(1)]_{C_2} .$$



Now, there is a way to make  $F(x, y)$  an exact differentiable function.

Let us work with a differential equation in the variables  $y(x)$  and  $x$ .

$$y' = \frac{dy}{dx}, \text{ or}$$

$$y'g(x, y) + h(x, y) = 0 .$$

We would like to solve this equation and find a function  $F(x, y)$  such that

$$dF = g(x, y)dy + h(x, y)dx$$

or

$$\frac{d}{dx}F(x, y) = y'g(x, y) + h(x, y) .$$

The integrability of  $F$  implies that

$$\frac{dF}{dx} = \frac{\partial F}{\partial x} + \frac{\partial F}{\partial y} y' .$$

Comparing the two previous equations, we must have

$$g(x, y) = \frac{\partial F}{\partial y} \quad \text{and} \quad h(x, y) = \frac{\partial F}{\partial x} .$$

If  $F$  is integrable then

$$\frac{\partial}{\partial x} \frac{\partial F}{\partial y} = \frac{\partial}{\partial y} \frac{\partial F}{\partial x} \quad \text{or} \quad \frac{\partial}{\partial x} g(x, y) = \frac{\partial}{\partial y} h(x, y) .$$

As an example, let us start with the equation

$$y'(xy - x^2) + (y^2 - 3xy - 2x^2) = 0 .$$

So,  $g(x, y) = xy - x^2$  and  $h(x, y) = y^2 - 3xy - 2x^2$ . Obviously,

$$\frac{\partial}{\partial x} g(x, y) \neq \frac{\partial}{\partial y} h(x, y) .$$

Thus, the integrability condition is not fulfilled. But if we multiple  $g(x, y)$  and  $h(x, y)$  by the function  $u(x, y) = 2x$ , and call  $G(x, y) = ug(x, y)$  and  $H(x, y) = uh(x, y)$ , then

$$\frac{\partial}{\partial x} G(x, y) = \frac{\partial}{\partial y} H(x, y) .$$

Thus, the function  $F$ , such that

$$\frac{dF}{dx} = y'G(x, y) + H(x, y)$$

is differentiable. In other words,

$$dF = \frac{\partial F}{\partial x} dx + \frac{\partial F}{\partial y} dy \equiv H dx + G dy .$$

# Chapter 4

## The Second Law of Thermodynamics

Assume a function  $f(x, y)$  is non-integrable such that

$$\frac{d}{dx}f(x, y) = h(x, y) + y'g(x, y)$$

or

$$df(x, y) = h(x, y)dx + g(x, y)dy .$$

But also assume that  $F = f(x, y)u(x, y)$  is integrable. In other words,  $u(x, y)$  makes  $f(x, y)$  integrable. If we identify the value of the heat supply to the system  $Q$  with the function  $f$  and write it as  $dF = \frac{dQ}{T}$ , where  $\frac{1}{T}$  plays the role of the function  $u$ , then  $F$  becomes an integrable function that we will call  $S$ , the entropy of the system:

$$dS = \frac{dQ}{T} .$$

From the thermodynamical point of view, this equality holds only if the process is reversible. The second law of thermodynamics says that in any other case,

$$dS > \frac{dQ}{T} .$$

In particular, if the system is cooled by a reversible process, i.e., in a quasistatic process at constant temperature, the entropy decreases. In an adiabatic process the entropy remains constant,  $dS = 0$ .

Before we continue with defining the other thermodynamic quantities and giving examples of their use, we should notice that besides the energy supplied to the system by heat and by work, there are other chemical and

physical fields that may act on the element of the system of mass, say  $dm_i$ , that are represented by  $\xi_i$ : we call them pseudopotentials (per unit mass). They could be of an electromagnetic nature or more complex chemical interactions. Thus, the First Law can be rewritten as

$$dU = dQ - dW + \xi_i dm_i$$

and the Second Law as

$$dS = \frac{dQ}{T} = (dU + dW - \xi_i dm_i) \frac{1}{T} .$$

The repeated index  $i$  means summation on all possible potentials  $\xi_i$  and elements of the system  $dm_i$ .

## Chapter 5

# The Third Law of Thermodynamics

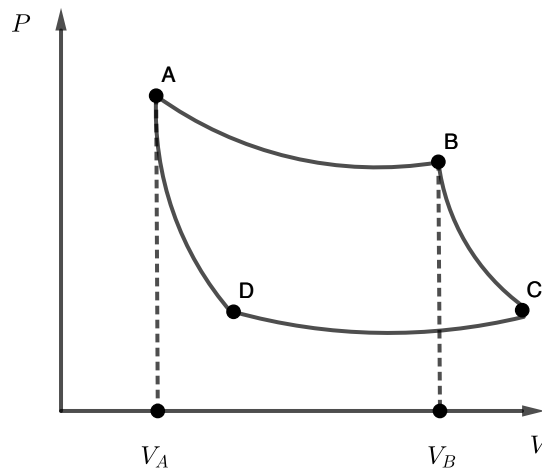
The Third Law says that the entropy  $S$  is zero at the absolute temperature  $T_0 = 0 = -273$  Celsius. That is,

$$S_{T_0} = 0 .$$

# Chapter 6

## The Carnot Cycle and the Second and Third Laws

The second law says that  $S > \frac{Q}{T}$  in an irreversible process. The third law says that  $S = 0$  when  $T = 0$ . In a reversible process,  $S = \frac{Q}{T}$ . One such reversible process is the Carnot cycle.



The gas goes through

1. Thermal expansion from  $A$  to  $B$  as it gains heat  $Q_M$ .

2. An adiabatic expansion (no heat exchanged) from  $B$  to  $C$  as it goes from temperature  $T_M$  to  $T_m$ .
3. A compression at constant temperature  $T_m$  from  $C$  to  $D$  in which it loses heat  $Q_m$ .
4. An adiabatic compression (no heat exchanged) from  $D$  back to  $A$  as it goes back to temperature  $T_M$ .

The work done from  $A$  to  $B$  is

$$W_{AB} = \int_A^B P dV = nRT_M \int_A^B \frac{dV}{V} = nRT_M [\ln V]_A^B$$

Also,

$$W_{AB} = [Q(T) - U(T)]_A^B = Q_{AB} = Q_M .$$

Because  $U$  does not change,  $U$  depends only on the temperature in an ideal gas. Thus,

$$Q_M = nRT_M \ln \frac{V_B}{V_A} .$$

Similarly,

$$Q_m = nRT_m \ln \frac{V_C}{V_D} .$$

For the adiabatic paths  $B - C$  and  $D - A$  and an ideal gas,

$$P_C V_C^\gamma = P_B V_B^\gamma$$

where  $\gamma = \frac{C_P}{C_V}$ .

The efficiency  $\eta$  of the cycle is given by

$$\eta = \frac{W}{Q_M} .$$

By energy conservation,  $W + Q_m = Q_M$ , so

$$\eta = \frac{Q_M - Q_m}{Q_M} = 1 - \frac{Q_m}{Q_M} .$$

In order to calculate  $\frac{Q_m}{Q_M}$ , we observe that in an adiabatic process the following are true:

$$P_B V_B^\gamma = P_C V_C^\gamma \quad \text{and} \quad P_D V_D^\gamma = P_A V_A^\gamma . \quad (6.1)$$

But since we are dealing with an ideal gas,

$$P_A V_A = P_B V_B \quad \text{and} \quad P_C V_C = P_D V_D$$

and

$$\frac{P_A V_A}{T_M} = \frac{P_D V_D}{T_m} \quad \text{and} \quad \frac{P_B V_B}{T_M} = \frac{P_C V_C}{T_m} . \quad (6.2)$$

From (6.1) and (6.2),

$$V_B^{\gamma-1} T_M = V_C^{\gamma-1} T_m$$

and

$$V_A^{\gamma-1} T_M = V_D^{\gamma-1} T_m .$$

Eliminating temperature,

$$\left(\frac{V_B}{V_A}\right)^{\gamma-1} = \left(\frac{V_C}{V_D}\right)^{\gamma-1}$$

or

$$\frac{V_B}{V_A} = \frac{V_C}{V_D} .$$

So from the expression of  $Q_M$  and  $Q_m$ ,

$$\frac{Q_M}{T_M} = \frac{Q_m}{T_m}$$

or

$$\eta = 1 - \frac{Q_m}{Q_M} = 1 - \frac{T_m}{T_M} .$$

The Carnot engine efficiency cannot be superseded by any engine that operates between two given temperatures  $T_M$  and  $T_m$ . In other words, all engines that convert heat into work will have  $\eta \leq \eta_{Carnot} = 1 - \frac{T_m}{T_M}$ . This is called the Carnot theorem.

As we have seen in the Carnot cycle,

$$\frac{Q_M}{T_M} = \frac{Q_m}{T_m} .$$

Since the entropy  $S$  is defined as  $dS = \frac{dQ}{T}$ , and  $Q_M$  and  $Q_m$  are delivered at constant temperature, then

$$S_M = \frac{Q_M}{T_M} \quad \text{and} \quad S_m = \frac{Q_m}{T_m} .$$



This tells us that in a Carnot cycle the heat is delivered at the same entropy found at the exhaust.

Kelvin and Planck expressed the second law of thermodynamics by saying that  $T_m$  could not ever reach the value of absolute zero in any real machine. In other words, there is no machine with 100% efficiency.

The efficiency of an irreversible process is always less than or equal to that of a reversible process,  $\eta_{irr} \leq \eta_{rev}$ , which means that

$$\left(\frac{Q_m}{Q_M}\right)_{irr} \geq \left(\frac{Q_m}{Q_M}\right)_{rev} = \frac{T_m}{T_M}.$$

Thus,

$$\left(\frac{Q_m}{T_m}\right)_{irr} \geq \left(\frac{Q_m}{T_M}\right)_{irr}.$$

Assuming the same working temperature for the irreversible process as the reversible one,

$$(S_m)_{irr} \geq (S_M)_{irr}.$$

In other words, the entropy at the exhaust point is greater than or equal to the entropy at the high temperature reservoir. Making another assumption that the reversible and irreversible cycles work with the same heat input and the same temperatures  $T_m$  and  $T_M$ , then

$$(Q_m)_{irr} > (Q_m)_{rev}.$$

Dividing both sides by  $T_m$ ,

$$\left(\frac{Q_m}{T_m}\right)_{irr} > \left(\frac{Q_m}{T_m}\right)_{rev}$$

or

$$S_{irr} > S_{rev}$$

which is another way to express the Second Law. This can be seen by calling  $(Q_m)_{rev}$  just  $Q$  and  $(T_m)_{rev}$  just  $T$ :

$$S_{irr} > \frac{Q}{T}.$$

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