

# **THE BASES OF CHEMICAL THERMODYNAMICS**

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**Volume 1**

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**THE BASES OF CHEMICAL THERMODYNAMICS**  
**Volume 1**

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# Preface

Our aim, in writing this two volume textbook, is to provide a simple yet logical treatment of the bases of Chemical Thermodynamics. It is our experience that the level of understanding improves when appropriate justifications are generously provided. In the many years that this course has been taught, we have endeavored to find the most easily grasped explanations or justifications.

Volume 1 presents the fundamental aspects of thermodynamics. It is designed to be appropriate for a first contact with the topic of thermodynamics. We illustrate the first and second laws of thermodynamics, the need to define the thermodynamic temperature scale, and the nature of entropy. We show how spontaneous processes always correspond to an increase of the global entropy. We explore the meaning of auxiliary thermodynamics functions, the origin and usefulness of partial molar quantities. We look into the description of gaseous systems and phase equilibria in systems where chemical reactions do not take place.

Volume 2 contains the tools that are necessary to deal with systems where chemical reactions take place. The variables of reaction are a key to this understanding. Criteria for chemical equilibrium and spontaneity of reactions are established. We illustrate how chemical reactions can provide work as, for example, in batteries. We analyze the effect of external factors on chemical equilibria.

We finally present the more complex situation of solutions, going from ideal to real solutions. The statistical aspect of thermodynamics

and its importance are stretched and examined in the last chapter with many illustrative problems.

Most of the specific mathematical tools are presented either directly in the text if they are used mostly in one chapter, while material needed in several chapters is included in an appendix.

We have purposely kept intermediate steps in the derivations to enhance the clarity of the presentation.

To keep the topic easily accessible to beginners, we selected a primarily phenomenological approach.

Teachers may wish to include some of the problems provided as part of their lectures to illustrate points that they consider particularly important.

Students will definitely appreciate the problem sections where full solutions to the problems are provided to enhance the pedagogical value of this book.

Finally, it is a pleasure to thank here our colleagues who have contributed to improve this work by their varied comments and suggestions, Dr. G. Rothenberger and Dr. D. B. Matthews. Professor A. Wohlhauser provided invaluable help in the treatment of independent reactions. In the course of time, students and assistants have contributed to improve this book by their comments, suggestions and constructive criticisms. Finally, we thank the many individuals who read the final version of the manuscript helping to remove so many unaesthetic details.

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# 1 Thermodynamic Systems : Definitions

## 1.1 Introduction

The origin of thermodynamics lies in the study of the relations that exist between mechanical systems and heat. As the understanding of the chemical and electrical phenomena improved with time, the domain covered by thermodynamics expanded to include all physical and chemical processes that involve energy conversion. The goal we pursue in writing this book, is to study thermodynamics and its application to the understanding of chemical reactions. As we shall see, heat exchange, temperature and pressure play a fundamental role as far as the evolution of chemical systems is concerned.

Thermodynamics has the advantage of providing macroscopic information without requiring a detailed knowledge of the microscopic state of the systems under investigation. Thus, one can obtain information on whether certain chemical reactions are possible or impossible. One can determine if a state is or is not a state of equilibrium or obtain limiting values for some of the quantities that vary during a process. If a change can indeed be achieved from a thermodynamic point of view, other effects, such as those involving kinetically controlled processes, may totally prevent a system from evolving towards its equilibrium state. Space or time dependent heat transfer processes or heat conduction will not be investigated here.

## 1.2 Interactions of Thermodynamic Systems with their Environment

We will be led to investigate thermodynamic systems (bodies or ensemble of bodies) which, due to their very nature will be in contact with other systems in various ways. According to the problem at hand, what constitutes the system and what constitutes its environment has to be stated to remove any ambiguity. It is useful to classify systems with respect to the exchanges that may take place in three different categories.

- Isolated systems

In an isolated system, any modification of the environment has no effect on the system, and any change of the system has no effect on the environment either. Neither matter, nor energy in any form are exchanged between the environment and the system.

- Closed systems

A closed system is a system which may exchange energy in any form with the environment (work, heat...) but which cannot exchange any matter. We should note here that this does not preclude the possibility that chemical processes can take place inside the system (Internal chemical processes).

- Open systems

An open system can exchange both energy and matter with its environment.

The previous definitions are summarized in Table 1.1.

	Exchange with the environment		
	Matter	Heat	Work
Isolated	No	No	No
Closed	No	Yes (a) No (b) }	Yes
Open	Yes	Yes	Yes

(a) Systems with diathermal walls.

(b) Systems with adiabatic walls.

**Table 1.1** Possible exchanges between a system and its environment.

### 1.3 System in a State of Equilibrium

A system is considered at equilibrium when no change takes place in it on a macroscopic scale, as time evolves. A small external perturbation is of no consequence to the system which returns to its equilibrium state when the perturbation ceases. We should point out here that, in some cases, some state, known as a *metastable state*, can exist even though such a state is not an equilibrium state from a thermodynamic point of view. Such a system should spontaneously evolve towards its equilibrium state, but for reasons that can be varied in nature, the expected evolution does not take place. In some instances, a small external perturbation may cause a spontaneous irreversible evolution towards a stable equilibrium state.

For a system to be at thermodynamic equilibrium, *mechanical equilibrium* must always be achieved. The vectorial sum of all mechanical forces applied to it must be zero.

If the system includes a gaseous phase<sup>†</sup>, its pressure has to be uniform.

*Thermal equilibrium* implies that temperature is the same at any point in the system.

A *chemical system* is at equilibrium if there are no variations of the composition of the system, in spite of the fact that local concentrations of some of the constituents may vary in a noticeable way in the various parts that make up the system.

We will deal with *homogeneous systems*, which have only one phase where the intensive variables<sup>††</sup> of the system ( $T$ ,  $p$ , composition of the system...) are uniform. We will also deal with *heterogeneous systems* where some of the intensive variables (composition of the system, specific weight...) may not be uniform.

A system is not at mechanical equilibrium if the sum of all mechanical forces applied to it is not zero.

If the pressure in the gas phase of a system is not uniform, gas movements will tend to take place.

If the temperature is not uniform, heat exchange will take place between various parts of the system.

If a system has not reached its chemical equilibrium, reactions will tend to take place and the concentration of some of the species will change with time. These reactions can be accompanied by energy exchanges of various forms.

---

<sup>†</sup> A precise definition of a phase will be given in chapter 8.

<sup>††</sup> See § 1.6 for the definition of an intensive variable.

## 1.4 Thermal reservoir. Heat Source.

We will call *thermal reservoir*, a heat reservoir that stays at a constant temperature  $T$ , under all circumstances. Moreover, it can exchange energy (with the system) *exclusively* in the form of heat. Its heat capacity is conceptually infinite. This means that a thermal reservoir remains at a constant temperature whatever the amount of heat it exchanges with a system. Such a thermal reservoir can therefore not be found in our real environment.

We will reserve the denomination *heat source* for a heat reservoir of finite heat capacity. A heat source with a very large heat capacity with respect to that of the system can be considered in general as a good approximation of a thermal reservoir. In practice, the temperature of a real heat source can be kept constant by supplying it with heat via some external means or by withdrawing heat from it.

## 1.5 Diathermal and Adiabatic Enclosures

A *diathermal enclosure* permits heat exchange between a system and its environment.

An *adiabatic enclosure* prevents any heat exchange between a system and its environment. We can mention two modes for heat exchange :

- *via electromagnetic radiation.* Matter emits and absorbs electromagnetic radiation. Radiation can be sopped by means of a reflective wall.
- *via conduction or convection.* These energy exchanges take place via microscopic motion or via macroscopic motion of matter respectively. Conduction can be prevented by a high vacuum between two walls.

## 1.6 State Function and State Variables. Intensive and Extensive Variables.

### 1.6.1 Definitions and Properties

The macroscopic state of a system is unequivocally defined by the knowledge of a certain number of state variables or state functions. Two

different kinds of variables are encountered : *Extensive variables* and *intensive variables*<sup>†</sup>.

- An *extensive variable* (or *property*) depends on the size of the system, for example  $U$ , the internal energy,  $H$ , the enthalpy,  $C_p$ , the heat capacity at constant pressure,  $C_V$ , the heat capacity at constant volume,  $S$ , the entropy,  $A$ , the Helmholtz energy,  $G$ , the Gibbs energy,  $V$ , the volume... Upon division of a system into several parts, an extensive property of the ensemble of the parts is the sum of the corresponding extensive property of each of the parts. Extensive properties of a system containing a pure species will be proportional to the number of moles of the species present.
- An *intensive variable* (or *property*) may have the same value in different subdivisions of a system. For example,  $p$ , the pressure,  $T$ , the temperature, are identical in all points of the system. Molar variables (properties) or partial molar variables, the specific mass, the refractive index, the molar heat capacity at constant pressure,  $C_{p,m}$ , have the same values in all points of one phase of the system. They may vary from one phase to another. If an intensive variable does not have the same value throughout a phase, then the system is not at equilibrium.

The number of variables needed to characterize the state of a system depends upon its nature. When we study in detail the *phase rule* (chapters 8 and 10), we will see how many intensive variables need to be known so that the other intensive variables are unequivocally determined.

For a system made up of a single chemical present as a single phase, only two intensive variables need to be known. Often one may select temperature and pressure as these two variables. The system will then be completely determined by knowing its mass or the number of moles in it. For a mixture of two chemicals that do not react and form a single phase, three intensive variables will need to be known. Knowledge of the pressure, temperature and mole fraction of one of the compounds will thus determine all of the intensive variables. The extent of the system can be known if the number of moles of one of its constituents is known.

The values of the state variables are independent of the ways by which the state may have been reached, and depend only on the state itself. We may consider *fundamental state variables or functions* such as  $U$ , the internal energy,  $V$ , the volume,  $S$ , the entropy,  $p$ , the pressure,

---

<sup>†</sup> See chapter 6 for an in-depth understanding of the mathematical properties of these variables.

$T$ , the temperature. *Auxiliary state variables or functions* ( $H$ , the enthalpy,  $A$ , the Helmholtz energy also known as the free energy,  $C_V$ , the heat capacity at constant volume,  $G$ , the Gibbs energy also known as the free enthalpy) are obtained from fundamental variables by simple mathematical operations (chapter 5 and 6). We have for example :

$$\left. \begin{aligned} H &= U + pV && \text{Enthalpy} \\ A &= U - TS && \begin{array}{l} \text{Helmholtz energy function} \\ \text{Free energy} \end{array} \\ G &= H - TS = U + pV - TS && \begin{array}{l} \text{Gibbs energy function} \\ \text{Free enthalpy} \end{array} \end{aligned} \right\} \quad (1.1)$$

All of the essential theoretical developments of thermodynamics could be developed in terms of the fundamental variables. Auxiliary variables are, however, much better suited for some of the applications. Some of the variables are obtained by differentiating other variables :

$$\left. \begin{aligned} \left( \frac{\partial U}{\partial T} \right)_V &= C_V && \text{heat capacity at constant volume} \\ \left( \frac{\partial H}{\partial T} \right)_p &= C_p && \text{heat capacity at constant pressure} \\ - \left( \frac{\partial U}{\partial V} \right)_{S, n_i} &= p && \text{pressure} \\ \left( \frac{\partial U}{\partial S} \right)_{V, n_i} &= T && \text{temperature} \end{aligned} \right\} \quad (1.2)$$

### 1.6.2 Isobaric Coefficient of Thermal Expansion. Isothermal Compressibility Coefficient

These coefficients are intensive variables obtained by differentiating the volume with respect to temperature or pressure (chapter 6). For a pure compound, present as a single phase, the volume may be expressed as a function of the variables  $p, T, n$  (number of moles).

$$V = V(p, T, n) \quad (1.3)$$

$$dV = \left( \frac{\partial V}{\partial T} \right)_{p, n} dT + \left( \frac{\partial V}{\partial p} \right)_{T, n} dp + \left( \frac{\partial V}{\partial n} \right)_{p, T} dn \quad (1.4)$$

For a condensed phase (liquid or solid), we define the *isobaric coefficient of thermal expansion*, also known as *isobaric expansivity*, the relative rate of change of the volume of the system with temperature.

$$\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_{p, n} \quad (1.5)$$

We also define the *isothermal compressibility coefficient*, the relative rate of change of the volume of the system with pressure :

$$\kappa = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_{T, n} \quad (1.6)$$

For a closed system, the number of moles does not vary ( $dn = 0$ ). One can write :

$$\left. \begin{aligned} dV &= \alpha V dT - \kappa V dp = V (\alpha dT - \kappa dp) \\ d \ln V &= \alpha dT - \kappa dp \end{aligned} \right\} \quad (1.7)$$

We just obtained an expression which allows us to calculate the variation of the volume of the system associated with an infinitesimal change in temperature and/or pressure, provided we know  $\alpha$  and  $\kappa$ . It may sometimes be useful to also consider the *constant volume thermal expansion coefficient* :

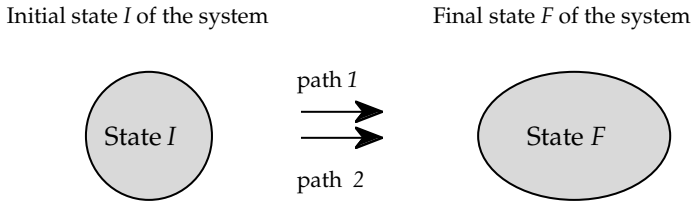
$$\beta = \frac{1}{p} \left( \frac{\partial p}{\partial T} \right)_{V, n} \quad (1.8)$$

## 1.7 Change of a State Variable as the Result of a Thermodynamic Process

### 1.7.1 General Process

We consider a change of a thermodynamic system from an initial state to a final state via two different paths, i.e. two different sequences of changes. Each of these changes is characterized by its own sequence of states (each characterized by values of some variables of state), that differ from one path to the other, but lead to the same final state (figure 1.2). Let  $X$  be a state variable which undergoes a variation during the process. The variation  $(X_F - X_I)$  does not depend on the path selected to perform the process :

$$(X_F - X_I)_{\text{path 1}} = (X_F - X_I)_{\text{path 2}} \quad (1.9)$$

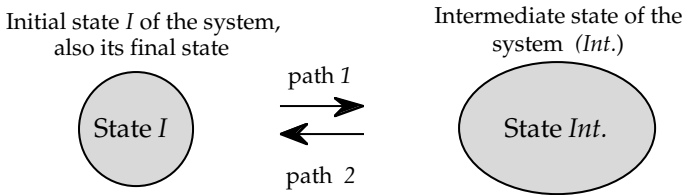


**Figure 1.2** Change of a system via two different paths.

The value of the state variable  $X$  depends only on the state itself, and not in the way it was reached.

### 1.7.2 Cyclic Process

We now consider a thermodynamic change of a system which reaches an intermediate state via path 1. Then path 2 is selected to bring the system back to its initial state. The global change that we just realized is known as a *cyclic process*. Such a process is schematically represented in figure 1.3.



**Figure 1.3** Schematic representation of a cyclic process. The final state is identical to the initial state.

The variation of the state variable  $X$  is zero for such a process, since the system is back to its initial state, which we may write :

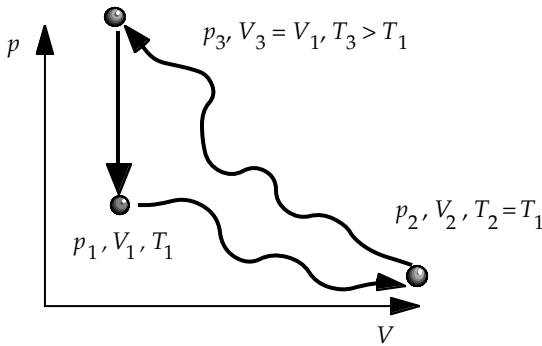
$$\oint dX = \int_I^{Int.} dX + \int_{Int.}^I dX = 0 \quad (1.10)$$

### 1.7.3 Expansion and Compression of a Gas

Figure 1.4 represents an example of a cyclic process of a gas where the initial state (1) and the final state are identical. Let us express the variation of the state variable *volume of the system* during this cyclic process.

$$\oint dV = \int_1^2 dV + \int_2^3 dV + \int_3^1 dV = (V_2 - V_1) + (V_3 - V_2) + (V_1 - V_3) = 0 \quad (1.11)$$

The line integrals indicate that the calculation has to be performed along the path represented by the curves on the figure. The system has the same volume at the end of the process as it did before it, and the variation of the volume is thus zero. The overall variation of any other state variable of this system is also zero.



**Figure 1.4** Example of a cyclic process.

A variable  $X$  (or a thermodynamic function) is a state variable (or state function) if its variation during a cyclic process is zero.  $X$  is also a state variable if its variation for a general process is independent of the means used to achieve this change as long as the initial and final states are identical. The *differential form*  $dX$  is said to be an *exact differential*. The line integral of an exact differential is independent of the path of integration. It depends only on the coordinates of the initial point (values of the variables used to define the initial state) and of the coordinates of the final point (values of the variables used to define the final state).

### 1.7.4 Mathematical Properties of a State Function

Let us assume that a state function  $X$  depends on the three variables of state  $x, y, z$ . Following a cyclic process, the variables  $x, y$  and  $z$ , go back to their initial values. The variation of  $X$  is thus zero for a cyclic process.

Let us examine the following differential expression :

$$dX = A dx + B dy + C dz \quad (1.12)$$

This differential expression is known as an exact differential expression if the following property holds :

$$dX = \left(\frac{\partial X}{\partial x}\right)_{y,z} dx + \left(\frac{\partial X}{\partial y}\right)_{z,x} dy + \left(\frac{\partial X}{\partial z}\right)_{x,y} dz \quad (1.13)$$

The integral of  $dX$  is  $X$ . The coefficients of  $dx, dy,$  and  $dz$  are identical in equations 1.12 and 1.13.

$$\left. \begin{aligned} A &= \left(\frac{\partial X}{\partial x}\right)_{y,z} \\ B &= \left(\frac{\partial X}{\partial y}\right)_{z,x} \\ C &= \left(\frac{\partial X}{\partial z}\right)_{x,y} \end{aligned} \right\} \quad (1.14)$$

According to *Schwarz theorem*, the second derivative of  $X$  with respect to two independent variables is independent of the order in which the derivations are performed. For the differential expression to be an exact differential expression, the following relationships must hold between its coefficients.

$$\left. \begin{aligned} \left(\frac{\partial A}{\partial y}\right)_{z,x} &= \frac{\partial^2 X}{\partial y \partial x} = \frac{\partial^2 X}{\partial x \partial y} = \left(\frac{\partial B}{\partial x}\right)_{y,z} \\ \left(\frac{\partial B}{\partial z}\right)_{y,x} &= \frac{\partial^2 X}{\partial z \partial y} = \frac{\partial^2 X}{\partial y \partial z} = \left(\frac{\partial C}{\partial y}\right)_{x,z} \\ \left(\frac{\partial C}{\partial x}\right)_{y,z} &= \frac{\partial^2 X}{\partial x \partial z} = \frac{\partial^2 X}{\partial z \partial x} = \left(\frac{\partial A}{\partial z}\right)_{x,y} \end{aligned} \right\} \Rightarrow \left\{ \begin{aligned} \left(\frac{\partial A}{\partial y}\right)_{z,x} &= \left(\frac{\partial B}{\partial x}\right)_{y,z} \\ \left(\frac{\partial B}{\partial z}\right)_{y,x} &= \left(\frac{\partial C}{\partial y}\right)_{x,z} \\ \left(\frac{\partial C}{\partial x}\right)_{y,z} &= \left(\frac{\partial A}{\partial z}\right)_{x,y} \end{aligned} \right\} \quad (1.15)$$

The integral of  $dX$  is then simply the function  $X$ , the value of which is only dependent on the values of the variables. The variation of  $X$  for a cyclic process is zero, and for any arbitrary change of the variables, it is independent of the path followed to realize the process.

## 1.8 Reversible and Irreversible Processes

We will have to envisage *reversible processes* which cannot exist in our real world but for which we will be able to obtain precise information on thermodynamic systems. Here are the *criteria for the reversibility* of a process.

A process is reversible if:

- *The intensive variables of the system ( $p$ ,  $T$ , chemical potentials) have a uniform value throughout the system<sup>†</sup>.*
- *There is only an infinitesimal difference between the forces generating a motion and the forces preventing it.*
- *Losses are negligible* (such as those due to friction, viscosity).
- *The process is carried out via a continuous sequence of equilibrium states.* In as much as an infinite time is necessary to achieve equilibrium, such a process can only be achieved at an infinitely slow rate.

*Real processes are always irreversible*, since they cannot rigorously satisfy any of the preceding criteria. A real process always has a finite rate, with dissipating effects, temperature gradients, finite rate of thermal exchanges, and a vessel wall that can never be totally adiabatic.

## 1.9 Equation of State

An equation of state is a relationship existing between some of the variables of state. For a system composed of a pure gas, the variables of state are the pressure,  $p$ , the volume,  $V$ , and the thermodynamic temperature,  $T$ , (§ 4.3.3). In this instance, the knowledge of these variables implies that the number of moles of gas present in a system is completely determined.

For example, for a pure ideal gas, the ideal gas law provides the number of moles via the relationship :

$$p V = n R T \quad (1.16)$$

where  $R$  is the *gas constant* ( $R = 8.314510 \text{ J K}^{-1} \text{ mol}^{-1}$ ). The pressure is expressed in units of Pascals (Pa), the volume in cubic meters ( $\text{m}^3$ ) and the temperature in kelvin (K).

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<sup>†</sup> If several phases are at equilibrium (heterogeneous system) the composition of the different phases may be different.



# 2 Work

## 2.1 Introduction

When chemical reactions take place, a certain amount of energy can be released and produce, for example, some mechanical work in a combustion engine, or some electrical work by means of a battery powered device. Thermodynamics is a science that allows a rational and quantitative study of these phenomena.

## 2.2 Sign Convention

When a thermodynamic system *receives* energy in any form, it is counted as a positive quantity. Reciprocally, when a system gives up energy to some part of its surroundings, then it is counted as a negative quantity. In thermodynamic studies, the laws are always expressed in such a way that the sign of the energy exchanges are always accounted for from the system point of view, whatever the system might be. This sign convention is now universally adopted for its simplicity and ease of use.

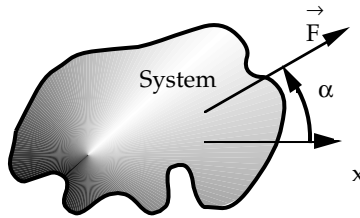
## 2.3 Mechanical Work

### 2.3.1 Definition

Let us consider a system submitted to an *external force*,  $\vec{F}$ , (Figure 2.1). When the application point of the force moves by an amount  $d\vec{x}$ , along the  $x$  axis, the mechanical work received (algebraically) by the system is given by :

$$\left. \begin{aligned} dw &= \vec{F} \cdot d\vec{x} \\ dw &= |\vec{F}| \cos \alpha dx \\ w &= \int_{x_1}^{x_2} |\vec{F}| \cos \alpha dx \end{aligned} \right\} \quad (2.1)$$

for a finite displacement from  $x_1$  to  $x_2$  along the  $x$  axis



**Figure 2.1** System submitted to an external force.

Let us note here that the elementary work  $dw$  expressed in equation 2.1 has the appropriate sign with respect to the sign convention that we have expressed in § 2.2.

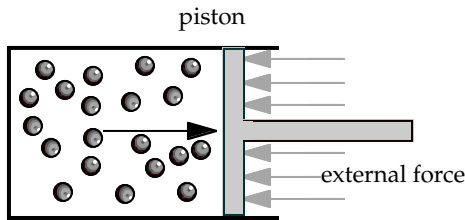
- If the external force vector  $\vec{F}$  has a component in the same direction as the displacement taking place, then the corresponding elementary work is positive. The system receives work.
- If the external force vector  $\vec{F}$  has a component in the opposite direction with respect to the displacement, then the corresponding elementary work is negative, and the system gives energy to the surroundings.

### 2.3.2 Work and Volume Change

We are now going to examine the exchange of work related to the increase or decrease of the volume of a system. This represents a particular case of mechanical work.

#### 2.3.2.1 Volume Increase, Expansion

When the volume increases during the process, the gas is said to undergo an expansion. It can be the case when a chemical reaction takes place and leads to an increase in the number of moles of gas present (at constant pressure).



**Figure 2.2** Gas inside a tank closed by a piston. The external force may be caused by some pressure.

Let us consider a *system* made up of a gas contained in a cylindrical container closed by a piston of area  $A$ . Whatever does not belong to the system is called the *environment* or the *surroundings* of the system. Let us assume that the only *external force* exerted on the piston is due to the external pressure as depicted in Figure 2.2. If the pressure  $p_{\text{int}}$  is larger than the pressure  $p_{\text{ext}}$ , the piston will have a spontaneous tendency to move to the right. The force exerted by the surroundings onto the piston has magnitude  $p_{\text{ext}} A$ . This force is directed towards the left. For an infinitesimal displacement  $dx$ , the system does work on the surroundings;  $dw$  is negative. We can write :

$$\left. \begin{aligned}
 |\vec{F}| &= p_{\text{ext}} A \\
 &\text{opposite to the direction of the displacement} \\
 dw &= -p_{\text{ext}} A dx = -p_{\text{ext}} dV \\
 dV &= A dx \\
 &\text{volume increase during the process} \\
 dx > 0 &\Rightarrow dV > 0
 \end{aligned} \right\} \quad (2.2)$$

### 2.3.2.2 Volume Decrease, Compression

Let us consider a gas undergoing a compression. Such a process will have the tendency to take place spontaneously if the pressure  $p_{\text{int}}$  is less than the outside pressure  $p_{\text{ext}}$ . In this case, work is done on the system by the surroundings, since the displacement takes place in the same direction as the external force. The same formula as above can be used;  $dw$  is positive, since the variation of the volume is, this time, negative.

$$\left. \begin{aligned}
 |\vec{F}| &= p_{\text{ext}} A \\
 &\text{same direction as the displacement} \\
 \\
 dw &= -p_{\text{ext}} A dx = -p_{\text{ext}} dV \\
 \\
 dV &= A dx \\
 &\text{decrease of the volume during the process} \\
 dx < 0 &\Rightarrow dV < 0
 \end{aligned} \right\} \quad (2.3)$$

### 2.3.3 Examples

#### 2.3.3.1 Process at Constant External Pressure

Let us envisage the case where a gas expands ( $p_{\text{ext}} < p_{\text{int}}$ ), while the outside pressure  $p_{\text{ext}}$  remains constant. The work received by the system during such a transformation is :

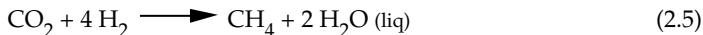
$$w = - \int_{V_I}^{V_F} p_{\text{ext}} dV = -p_{\text{ext}} \int_{V_I}^{V_F} dV = -p_{\text{ext}} (V_F - V_I) \quad (2.4)$$

It can be seen that the work received by the system *depends on the external pressure*, i.e. the outside, and does not depend on the inside pressure of the system. For the expansion under study, negative work is done on the system, the final volume,  $V_F$  being larger than the initial volume,  $V_I$ .

As a particular case, we can examine an experiment where the external pressure is zero,  $p_{\text{ext}} = 0$ . The work done on a system during such a process is zero. The same formalism can be applied to a compression at constant external pressure, since we did not really make use of the fact that we were studying an expansion. The work done on the system will, however, be positive in this eventuality.

### 2.3.3.2 Volume Work during Chemical Reactions

Let us consider a system made up of one mole of  $\text{CO}_2$  and four moles of  $\text{H}_2$  at  $25^\circ\text{C}$  under atmospheric pressure. Assume that the following reaction takes place at constant pressure and temperature.



Let us evaluate the work done on the system when the reaction has proceeded completely from left to right. The pressure is still one atmosphere and the temperature  $25^\circ\text{C}$ . Here we only consider the work due to the change in the volume of the system, and ignore the energetics of the chemical reaction. The volume work is given by :

$$w = -p_{\text{ext}} (V_F - V_I) \quad (2.6)$$

Let us use, as a good approximation, the equation of state for an ideal gas and neglect the volume of the liquid water formed in the reaction with respect to the final gas volume. We obtain :

$$p_{\text{ext}} V_I = 5 R T \quad p_{\text{ext}} V_F = R T \quad (2.7)$$

$$w = 4 R T = 4 \text{ mol} \cdot 8.31 \text{ J K}^{-1} \text{ mol}^{-1} \cdot 298 \text{ K} = 9906 \text{ J}$$

### 2.3.3.3 Work during an Isothermal (Reversible) Change of an Ideal Gas

During an *isothermal change*, the temperature of the system stays constant and is the same at every point. For a system where a mechanical process is the only process that can take place, such a process is possible only if it is *reversible*.<sup>†</sup> Let us consider a (*reversible*) *isothermal expansion* of a gas confined in the system depicted in figure 2.2. This process is a *continuous succession of equilibrium states*. The volume of the gas varies from volume  $V_I$  to volume  $V_F$ . The external force applied to the piston in every intermediate state exactly compensates the force due to the internal pressure of the system since each of these states is a state of equilibrium. We can imagine that we apply at every instant an external pressure,  $p_{\text{ext}}$  equal to  $p_{\text{int}}$ . The external pressure is slowly decreased in such a way as to be only marginally smaller than the

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<sup>†</sup>An isothermal yet irreversible process can be imagined. Consider a system where a chemical reaction can spontaneously, thus irreversibly, take place. Such a process can indeed be isothermal if heat exchanges are sufficiently fast compared to the rate of the reaction.

internal pressure. (This could be practically realized by placing the cylinder in a vertical position, with appropriate little masses placed on it. Then, one could slowly remove small fractions of these masses). Under these conditions, the work done on the gas for an infinitesimal process is given by:

$$dw = -p_{\text{ext}} dV = -p_{\text{int}} dV \quad (2.8)$$

We can easily obtain a formal result for a *finite isothermal (reversible) process of an ideal gas*. The ideal gas law can be used since, at every moment, the gas is at equilibrium. The internal pressure  $p_{\text{int}}$  can be expressed as a function of the volume of the gas. The expression for the work received by the gas is:

$$w = - \int_{V_I}^{V_F} \frac{n R T}{V} dV = -n R T \int_{V_I}^{V_F} \frac{dV}{V} = -n R T \ln \left( \frac{V_F}{V_I} \right) \quad (2.9)$$

The same expression would be obtained for an isothermal compression.

#### 2.3.3.4 Remarks

For systems interacting with a force field, the gravity field for example, it is necessary to perform a global balance of the *external forces* acting on the system. Work is algebraically done on the system upon displacement of the point where an external force is applied to it.

It is important to mention that a reversal of the displacement direction keeping all external forces unchanged, implies a change of the sign of the work done on the system. For a finite process, a change in the sign of each elementary displacement, while the system goes through the same intermediate states (identical forces), defines a new process referred to as the *reverse process*. The work done on the system during the reverse process is therefore opposite to that done on it during the direct process.

## 2.4 Electrical Work

A battery can transform potential chemical energy into electrical work. The chemical reaction is carried out at electrodes. A voltage  $E$  exists between the positive and the negative poles of the battery.  $E$  is

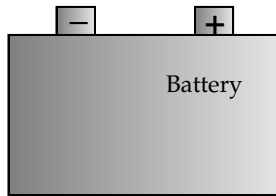
known as the *source voltage* or the electromotive force (e.m.f.) and it is defined to always be positive. It corresponds to the potential difference between the potential of its positive pole  $\phi_+$  and that of its negative pole  $\phi_-$  :

$$E = (\phi_+ - \phi_-) \quad (2.10)$$

The values for the potentials  $\phi_+$  and  $\phi_-$  depend on an arbitrary reference potential while  $E$  does not depend on this reference. Consider a charge  $dQ$ , supplied, for example by a battery, going from a potential  $\phi_+$  to a potential  $\phi_-$  ( $\phi_+ > \phi_-$ ). The work done on the system (the battery) is :

$$dw = - (\phi_+ - \phi_-) dQ = -E dQ \quad (2.11)$$

A positive charge that moves from the positive pole + (high potential), through the external circuit, to the negative pole - (low potential) implies that work is delivered by the system to the outside. This corresponds to the normal operation of a battery.



**Figure 2.3** A battery.

A positive charge going from the negative pole - (low potential), through the external circuit, to the positive pole + (high potential) corresponds to work received by the battery. In this charging process, energy is stored in the battery under a chemical form. The electric potential (the voltage) has units of Volts (V) and the charge has units of Coulombs (C). The charge of one mole of a singly charged ion is 1 Faraday (F). ( $F = N_A e = 96485.309 \text{ C mol}^{-1}$ ).

## 2.5 Various Forms of Energy

Energy can be found in various forms. We may cite electrical, mechanical and thermal energy. Other forms have their origin in chemical, electromagnetic, gravitational and nuclear interactions.

## 2.6 Various Expressions for Work

For systems in which work has origins other than those mentioned until now, appropriate expressions must be used to express the work in each case. The work is always obtained as a scalar product of the force by an elementary displacement. However, specific formulas are used that involve appropriate intensive variables for the system under study.

Thus, if we increase by  $dA$  the area  $A$  of a system with interfacial tension  $\sigma$ , the work done on the system is :

$$dw = \sigma dA \quad (2.12)$$

For an increase  $dz$  of the altitude of an object of mass  $m$  in the gravity field  $g$ , the work done on the system is :

$$dw = m g dz \quad (2.13)$$

Lengthening an elastic material by  $dl$  under tension  $T$  does work on the system, given by :

$$dw = T dl \quad (2.14)$$

The work done on a substance in a magnetic field  $B$  with a magnetic moment  $dM$ , is :

$$dw = B dM \quad (2.15)$$

# 3 First Law of Thermodynamics

## 3.1 Introduction

One can experimentally observe energy exchanges between bodies and these exchanges can be classified according to the macroscopic nature of the interactions that take place.

As an example, a windmill moves under the action of the wind. The kinetic energy of the wind is transformed into mechanical work, the interaction being purely mechanical.

Heat exchange can take place between several parts of a system, as the heating of a pot of water over a fire. When several systems are in thermal contact for a long enough time, thermal equilibrium can be attained, all of the systems ending up at the same temperature. This can be observed when mixing hot and cold liquids, in which case the thermal contact is excellent.

Some phenomena involve simultaneous exchanges of heat and work. Frictional forces on solid surfaces give rise to dissipative phenomena which consist in the destruction of some form of mechanical energy to generate heat. The brakes of a vehicle transform its kinetic energy into heat.

Conversely, thermal engines, such as the steam engine, partially transform heat into mechanical energy.

We propose to describe here some of the experiments which have, in the past, provided the fundamental observations needed to formulate some of the rules applicable to these energy exchanges and that constitute the first law of thermodynamics.

## 3.2 The Joule Experiment

Around the middle of the 19<sup>th</sup> century, Joule demonstrated experimentally the equivalence between mechanical energy and heat by means of a series of experiments that are briefly described below.

A system containing water is surrounded by an adiabatic wall. A paddle wheel is operated by a weight falling in the gravity field of the earth. The temperature of the liquid rises due to the viscosity forces (friction) in the liquid. The temperature rise is directly related to the amount of work received by the system which corresponds to the decrease in the potential energy of the weight. Joule showed that the same temperature rise could be attained using an electrical resistor heated by electric current.

Using varied experimental conditions, Joule was able to show that the amount of work received by the system and the amount of heat needed to produce the same temperature rise are proportional. The conclusion was straightforward. Heat and work are of the same nature and constitute different forms of energy. They can therefore be expressed in the same units.

The joule (symbol J) is the SI unit of energy. Frequently one still encounters in practical applications the calorie (symbol cal) to express amounts of heat. One calorie corresponds to the amount of heat that is needed to get one gram of water from 14.5°C to 15.5°C. We have the equivalence  $1 \text{ cal} = 4.1840 \text{ J}$ .

## 3.3 Internal Energy. First Law

### 3.3.1 General Aspects. Expression of the First Law of Thermodynamics

Let us consider a thermodynamic system. By delivering to this system energy as heat and/or work, the system will evolve from an initial state  $I$  to a final state  $F$ . We define a function  $U$ , which we call the *internal energy*, that only depends on the state of the system. This function must account for all energy exchanges, relevant to the problem at hand, taking place between the system and its environment. The state of the system has to be characterized by a number of variables, called state variables, which we shall investigate later. In a significant number of instances, the potential energy of the system in the gravity field of the earth need not be taken into account. The effect of external fields or the variation of the kinetic energy of the macroscopic system must be

accounted for separately, but we do not envisage here cases where they need to be taken into account.

The first law of thermodynamics deals with the internal energy  $U$  and can be stated as:

*The internal energy of a system is a state function.*

An immediate consequence is that *the differential of the internal energy  $U$  is an exact differential.*

### 3.3.2 Application to a Closed System

#### 3.3.2.1 Adiabatic Process

Let us consider a *closed system* contained inside an adiabatic enclosure. The work done on the system during an adiabatic process corresponds to the change in its internal energy. This was the case in the Joule experiment. We can write :

$$U_F - U_I = w_{\text{adiabatic}} \quad (3.1)$$

The work done on a system during an adiabatic process is equal to the change of its internal energy  $U$ .

#### 3.3.2.2 General Process

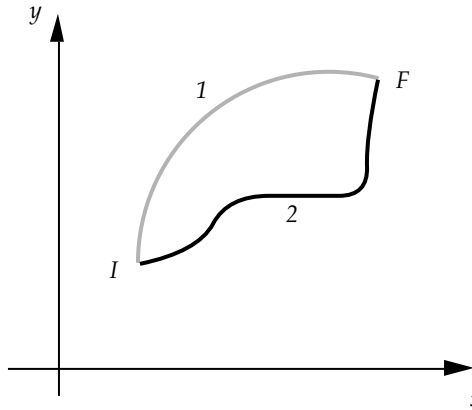
We now consider a system that can exchange energy with its environment as *work* or *heat*. We give in figure 3.1 a schematic representation of the process envisaged here in terms of two state variables  $x$  and  $y$ .

During a process, the state of the system is characterized at all stages by an appropriate number of state variables. Starting from its initial state  $I$ , the system goes through a number of intermediate states along path  $1$  to end up in its final state. The variation of the internal energy  $U$  during this process is :

$$U_F - U_I = w_1 + q_1 \quad (3.2)$$

Let us now assume that we know how to get the system from the same initial state  $I$  to the same final state  $F$  via a different path  $2$ . Since the internal energy  $U$  is a state function, the consequence of the first law is :

$$U_F - U_I = w_2 + q_2 = w_1 + q_1 \quad (3.3)$$



**Figure 3.1** Schematic representation of two different processes bringing a thermodynamic system from state  $I$  to state  $F$ , along two different paths.

The *first law* implies that the sum of the work and the heat received by the system is the same between two given states whatever method is used to achieve the change. We will find that, in general,  $w_1 \neq w_2$  and  $q_1 \neq q_2$ .

### 3.3.2.3 Cyclic Process

Let us consider a process that brings the system from state  $I$  to state  $F$  along path 1. Assume we can now continue the process by bringing the system, back to state  $I$ , along path 2 but in the direction ( $F \rightarrow I$ ). The global process is known as a cyclic process. During this cyclic process, the amount of work  $w$  is done on the system while an amount of heat  $q$ , is taken in by it. The corresponding variation of the internal energy is :

$$\Delta U = U_F - U_I + (U_I - U_F) = 0 = w + q \quad (3.4)$$

During a *cyclic process*, the variation of the internal energy  $U$  of a system is zero.

*The sum of the work and heat received by a system during a cyclic process is zero.*

### 3.3.2.4 Infinitesimal Process

The differential form of equation 3.3 is:

$$dU = dw + dq \quad (3.5)$$

and  $dU$  is an exact differential. The variation of the internal energy during an infinitesimal process of a closed system is the sum of the work and heat, it receives. The amount of heat and work received by a system are therefore not state variables. They depend on the way the process has been carried out. The differential forms  $dw$  and  $dq$  are not exact differentials. The result obtained by integrating  $dw$  or  $dq$  depends on the path selected to carry out the integration.

### 3.4 Internal Energy – A Look at the Molecular Scale

Let us study a system made up of gas molecules. These molecules are in constant motion. The energy of each single molecule is modified at every instant by means of collisions with other molecules or with the walls of the container. These changes take place in such a way that, on the macroscopic level, no change in the energy of the system takes place. It is impossible but also unnecessary to know the individual behavior of each molecule. However, for a system in thermal equilibrium, it is possible to determine the average number of molecules which, at any moment, have a given value of their energy. To achieve this goal, one uses *Statistical Mechanics*, with appropriate distribution laws and quantum mechanics to obtain with the help of the Schrödinger equation, the energy levels that are available to the molecules (See chapter 13).

Thus, for example, if the energy level  $\epsilon_1$  is occupied by  $N_1$  molecules, the internal energy of the system is given by :

$$U = \sum_i \overline{N_i} \epsilon_i \quad (3.6)$$

where the sum applies to all energy levels accessible to the molecules in the system. We will see in chapter 13 how it is possible to obtain some information on the properties of various systems with these methods.