

INTRODUCTORY THERMODYNAMICS

Pierre Infelta

**Swiss Federal Institute of Technology
Lausanne, Switzerland**

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Foreword

In numerous fields, a certain level of understanding of thermodynamics is a necessity, yet the amount of time imparted to this end is often very scanty. Hence, the need for a simple, compact and easy to read text, intended for students beginning in the field.

This textbook provides a very concise yet clear presentation of classical thermodynamics in 178 pages. I include many examples (111 actually) to provide instant illustrations and applications of the results obtained.

Being concise implies that the reader has to accept a number of properties without rigorous derivations, such as "Entropy is a state function". We all know, however, that a good understanding and logical derivations significantly decrease the amount of material that needs to be memorized. Whenever possible, I present many simple (often somewhat original) derivations with intermediate steps in the derivations. Equations, without clear statements giving the extent of their validity, are useless. I made a point to clearly mention, where needed, the conditions under which a relation is valid. I also include a very extensive index.

The *ebook* version is a very small file, instantly available for download. It is very useful for efficient searches, highlighting and writing notes and is enriched with colored figures.

I wish to express my thanks to the many colleagues, former colleagues and friends who have contributed so significantly to the quality of this book by their careful reading and their subsequent comments.

Pierre Infelta
School of Basic Sciences,
Swiss Federal Institute of Technology
Lausanne, Switzerland

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1. Thermodynamic Systems : Definitions

1.1 Interactions of Thermodynamic Systems with their Surroundings

A thermodynamic system is a part of the universe of interest, while anything else constitutes its surroundings. These two parts may be divided by a real boundary or an imaginary conceptual one. According to the problem at hand, what constitutes the system and what constitutes its surroundings needs to be clearly stated to remove any ambiguity. It is useful to classify systems with respect to the exchanges that may take place in three different categories.

	Exchange with the surroundings		
	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 surroundings.

1.2 Equilibrium

A state of equilibrium of a system is characterized by :

- Mechanical equilibrium
- Uniform pressure throughout the system
- Thermal equilibrium throughout the system
- Additionally for chemical systems : stationary concentrations for homogeneous systems or heterogeneous systems.

1.3 Thermal Reservoir. Heat Source

We often consider a *thermal reservoir*. It is a heat reservoir always at a temperature T that exchanges energy with its surroundings *exclusively* as heat. It can be approximated by a large heat capacity body or a system with phase equilibrium under a constant pressure. We also may discuss *heat sources*. They are heat reservoirs of finite heat capacity.

1.4 Diathermal and Adiabatic Enclosures

A diathermal enclosure allows heat exchanges to take place between a system and its surroundings. An adiabatic enclosure prevents heat exchanges between a system and its surroundings.

1.5 Zeroth Law of Thermodynamics

This law derives from empirical observations and is accepted as a fundamental postulate of thermodynamics. It can be formulated as follows :

- Two systems placed in contact via a diathermal wall will, given enough time, get in thermal equilibrium.
- If one system is in thermal equilibrium with two other systems, these two systems are also in thermal equilibrium with one another.

When systems are not in thermal equilibrium, heat transfer spontaneously takes place from the hottest to the coldest one. When systems are in thermal equilibrium, heat transfer no longer takes place. Using some appropriate thermometer, the temperatures of systems in thermal equilibrium are found to be identical.

1.6 Intensive and Extensive Variables. State Functions and State Variables

1.6.1 Definitions

The thermodynamics variables mentioned here will be defined in due course.

- An **Extensive variable** depends on the size of the system.

Examples of extensive variables are U , internal energy, H , enthalpy, C_p , heat capacity at constant pressure, C_V , heat capacity at constant volume, S , entropy, A , Helmholtz energy, G , Gibbs energy, V , volume... For a system consisting of 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 are proportional to the number of moles of the species present.

- An **Intensive variable** has a uniform value in different subdivisions of a system.

Examples of intensive variables are p , pressure, T , temperature, identical in all points of the system. Molar variables or partial

molar variables, specific mass, mole fractions, molar heat capacity at constant pressure, $C_{p,m}$, have the same values in all points of one phase of the system. They may differ from one phase[†] to another.

The number of intensive variables needed to characterize the state of a system depends upon its nature. See the **phase rule** (chapters 8 and 10).

For a system with a single chemical species present as a single phase only two intensive variables need to be known. The variables we just mentioned are called **state variables** or also **state functions**. They depend only on the state of the system and not on the way the state was reached.

1.6.2 Fundamental and Auxiliary State Variables or Functions

Examples of fundamental state variables or functions are U , internal energy, V , volume, S , entropy, p , pressure, T , temperature. Auxiliary state variables are obtained starting from the fundamental ones. Examples of auxiliary state functions are H , the enthalpy, A , the Helmholtz energy, C_V , the heat capacity at constant volume, G , the Gibbs energy. Sometimes, several names may be used for the same function. See their properties in chapters 5 and 6.

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

We will see that some of the variables are obtained by differentiating other variables :

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

[†] See chapter 8 for the definition of a phase.

1.6.3 Thermal Coefficients

Thermal coefficients indicate how volume or pressure is affected by a change in temperature. For a pure compound in a single phase, we have :

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

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

Isobaric coefficient of thermal expansion, or isobaric expansivity

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

Isothermal compressibility coefficient

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

For a closed system, $dn = 0$.

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

Constant volume thermal expansion coefficient

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

Example

Assume that α and κ are constant. By integration of the second Eq. of 1.7, we have :

$$\left. \begin{aligned} \ln \frac{V}{V_0} &= \alpha(T - T_0) - \kappa(p - p_0) \\ \Downarrow \\ V &= V_0 e^{\alpha(T - T_0) - \kappa(p - p_0)} \end{aligned} \right\}$$

Using as numerical values $\alpha = 2 \cdot 10^{-4} \text{ K}^{-1}$ and $\kappa = 4 \cdot 10^{-11} \text{ Pa}^{-1}$, let us find the volume, at 10^8 Pa and 800 K , of a liquid sample of 1 cm^3 at 10^5 Pa and 300 K . We have :

$$V = 10^{-6} e^{2 \cdot 10^{-4} \cdot (800 - 300) - 4 \cdot 10^{-11} \cdot (10^8 - 10^5)} \approx 1.047 \cdot 10^{-6} \text{ m}^3 = 1.047 \text{ cm}^3$$

The increase in temperature increases the volume of the sample, while the pressure increase, decreases it.

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

1.7.1 General Process

For a state variable, X , $(X_F - X_I)$ is independent of the path[†] used for the process. The intermediate states of the system are irrelevant.

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

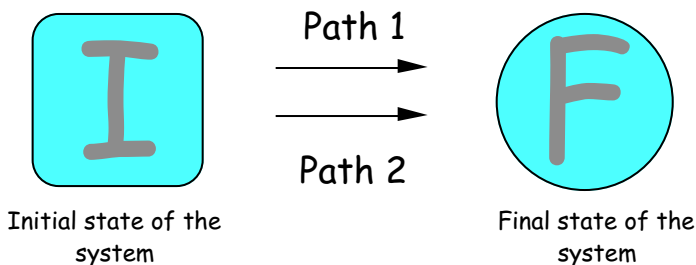


Figure 1.2 Change of a system via two different paths.

1.7.2 Cyclic Process

Consider a thermodynamic change of a system to some intermediate state via path 1. Then along path 2, bring the system back to its initial state. This process is a **cyclic process** (illustrated in figure 1.3). The change of X is zero for a cyclic process.

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

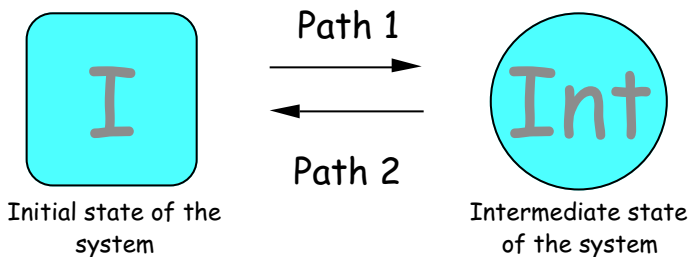


Figure 1.3 Schematic representation of a cyclic process.

[†] The path corresponds to a certain way of carrying out the process.

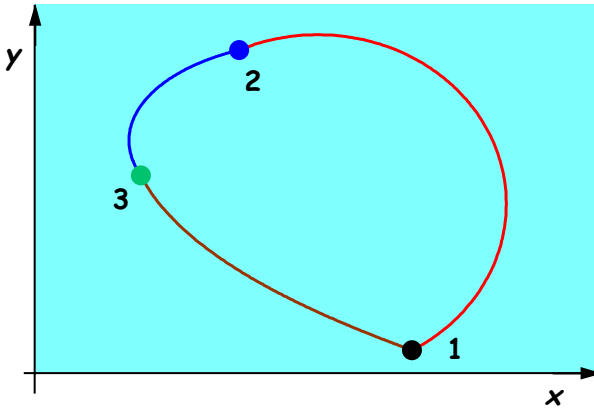


Figure 1.4 Example of a cyclic process. The variables that define the states in this case are x and y .

Example of a cyclic process: the initial state (1) and final state as displayed in Fig. 1.4 are identical.

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

There is no volume change. *The change of any state variable is zero for any cyclic process.*

A variable X is a state variable (or state function) if its change for a cyclic process is zero. X is also a state variable if its change for a general process depends only on the initial and final states of the system and not on the way the change is achieved. The differential form dX is then called an **exact differential**. The line integral of an exact differential is independent of the path of integration.

1.7.3 Mathematical Characteristics of a State Function

Consider the differential expression :

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

In this instance, X depends on the three variables of state x , y , z .

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

The integral of dX is X . We have :

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

According to **Schwarz theorem**, the second derivative of a state function X with respect to two variables is independent of the order in which the derivatives are calculated. The differential expression is exact if :

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

Example

Consider the function $F(x,y,z) = x^3 + 5x^2y - 2z^3x$. The differential dF is :

$$dF = (3x^2 + 10xy - 2z^3) dx + 5x^2 dy - 6z^2 x dz$$

The following second order differentials are equal :

$$\left(\frac{\partial^2 F}{\partial x \partial y} \right) = \frac{\partial}{\partial x} (5x^2) = 10x = \left(\frac{\partial^2 F}{\partial y \partial x} \right) = \frac{\partial}{\partial y} (3x^2 + 10xy - 2z^3)$$

1.8 Reversible and Irreversible Processes

A **reversible process** is carried out via a *continuous sequence of equilibrium states*.

- The intensive variables (p , T , chemical potentials) have a uniform value throughout the system.
- If and when the system is in contact with a thermal reservoir, the system temperature is equal to the temperature of the thermal reservoir.
- Losses are negligible (no friction, no viscosity).
- The forces applied to movable parts of the system are zero.

All other processes that can take place (any real processes) are **irreversible**.

1.9 Equation of State

An **equation of state** is a relationship between some of the variables of state of a pure species (usually a fluid) that completely defines the state of the system. For a pure gas: pressure, p , molar volume, V_m , and thermodynamic temperature, T . As an example, we have for a pure ideal gas:

$$p V_m = R T \quad \text{where} \quad V_m = \frac{V}{n} \quad (1.16)$$

$R =$ **gas constant** ($R = 8.314472 \text{ J K}^{-1} \text{ mol}^{-1}$), n is the number of moles of gas. The pressure is in Pascal (Pa), the volume in cubic meters (m^3), the temperature in kelvin (K).

2. Work

2.1 Sign Convention for Energy Exchange

When a thermodynamic system *receives energy* in any form, it is counted as a positive quantity. When a system *gives up energy* to some part of its surroundings, it is counted as a negative quantity. Thermodynamic laws are expressed in such a way that the sign of the energy exchanges are always accounted for from the system point of view. This sign convention is now universally adopted for its simplicity and ease of use. It is good practice to always consider algebraic thermodynamic quantities.

2.2 Mechanical Work

2.2.1 Definition

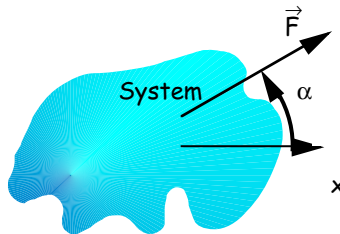


Figure 2.1 System submitted to an external force.

Consider a system submitted to an *external force*, \vec{F} . When the application point of the force moves by $d\vec{x}$, the algebraic mechanical work done on 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

The elementary work dw expressed in Eq. 2.1 has the appropriate sign with respect to the sign convention of § 2.1.

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.

Example

If the application point of a force of 10 N (the unit of force is the newton) is displaced 1 m in its direction (angle $\alpha = 0$), the work done, on the system it applies to, is :

$$w = 10 \cdot 1 = 10 \text{ J}$$

Energy is measured in joules, symbol J.

2.2.2 Work and Volume Change

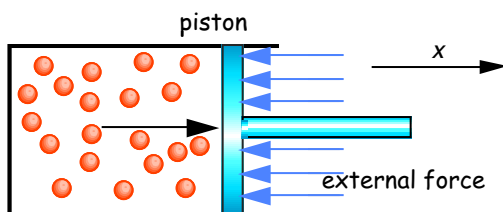


Figure 2.2 Gas inside a cylinder closed by a piston. The external force may be caused by a pressure.

The system is a gas in a cylinder closed by a piston of area A . Everything else is called the *surroundings* of the system. If V increases during the process, the gas is said to undergo an *expansion*. If V decreases during the process, the gas is said to undergo a *compression*. The *external force* exerted on the piston is due to the external pressure (Fig. 2.2).

If $p_{\text{int}} > p_{\text{ext}}$, the piston has a spontaneous tendency to move to the right, opposite to the external force. The magnitude of the external force on the piston is $p_{\text{ext}} A$ towards the left.

For $dx > 0$, the system does work on the surroundings, dw is negative.

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

A displacement in the direction of the external force occurs when $p_{\text{int}} < p_{\text{ext}}$, then $dx < 0$ and $dw > 0$. The expression for the (algebraic) work done by the system due to its change of volume is always valid.

2.2.3 Process at Constant External Pressure

The work done on the system during the process is:

$$w = - \int_{V_I}^{V_F} p_{\text{ext}} dV = - p_{\text{ext}} \int_{V_I}^{V_F} dV = - p_{\text{ext}} (V_F - V_I) \quad (2.3)$$

The work done on the system *depends on the external pressure*, i.e. the outside, and does not depend on the inside pressure of the system. If $p_{\text{ext}} < p_{\text{int}}$ and p_{ext} constant, we find:

$$V_F > V_I \Rightarrow w < 0 \quad \text{expansion}$$

$$\text{If } p_{\text{ext}} = 0 \text{ then } w = 0$$

Example

We can calculate the volume work done on a system during a chemical reaction that takes place at constant external pressure. Assume the following reaction is complete at 25 °C (298.15 K) and 10^5 Pa using an appropriate catalyst.



Starting with 0.5 mole of gas in stoichiometric proportion in the initial state, there is only 0.1 mole of gas when the reaction is complete (the water is liquid, its volume is negligible compared to the gas volume). Assuming that the gases obey the ideal gas law, the initial and final volumes of the system are:

$$V_I = \frac{n_I R T}{p} = \frac{0.5 \cdot 8.3145 \cdot 298.15}{10^5} \approx 12.39 \cdot 10^{-3} \text{ m}^3 = 12.39 \text{ l}$$

$$V_F = \frac{n_F R T}{p} = \frac{0.1 \cdot 8.3145 \cdot 298.15}{10^5} \approx 2.48 \cdot 10^{-3} \text{ m}^3 = 2.48 \text{ l}$$

The work done on the system is:

$$w = - p_{\text{ext}} (V_F - V_I) \approx - 10^5 (2.48 \cdot 10^{-3} - 12.39 \cdot 10^{-3}) \approx 991 \text{ J}$$

The surroundings do work on the system.

2.2.4 Work during an Isothermal (Reversible) Change of an Ideal Gas

During an *isothermal reversible change*, the temperature of the system stays *constant and uniform for the entire process* which takes place as a *continuous succession of equilibrium states*.

The gas volume varies from V_I to 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. We apply at every instant an external pressure, $p_{\text{ext}} = p_{\text{int}}$. For an infinitesimal process, the work done on the system is given by:

$$dw = - p_{\text{ext}} dV = - p_{\text{int}} dV \quad (2.4)$$

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 expression for the work done on the gas is :

$$w = - \int_{V_I}^{V_F} \frac{n R T}{V} dV = - n R T \int_{V_I}^{V_F} \frac{dV}{V} = - n R T \ln \left(\frac{V_F}{V_I} \right) \quad (2.5)$$

Example

We can calculate the volume work done on one mole of an ideal gas when its volume doubles during an isothermal change of volume at 500 K.

$$w = - 1 \cdot 8.3145 \cdot 500 \cdot \ln 2 \approx - 2881 \text{ J} \approx - 2.88 \text{ kJ}$$

Since w is negative, the gas does work on the surroundings.

2.3 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.
- Consider a *reversible process*. 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 often 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*. The change in the internal energy of the system in the reverse process is opposite to the change in the direct process, which finally implies (See Chapter 3, The First Law) also that the heat received by the system is opposite to that received in 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 via redox processes. The *source voltage* E (electromotive force - e.m.f.) is defined to always be positive.

$$E = (\phi_+ - \phi_-) \quad (2.6)$$

E does not depend on the reference for the potentials ϕ_+ and ϕ_- . The work done on the battery when a charge dQ goes from a potential ϕ_+ to a potential ϕ_- ($\phi_+ > \phi_-$) is:

$$dw = -(\phi_+ - \phi_-) dQ = -E dQ \quad (2.7)$$

For dQ positive, dw is negative, work is done by the battery on the outside. This corresponds to the normal operation of a battery.

In the charging process, dQ is negative. Energy is stored in the battery in 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, $F = N_A e = 96485.3415 \text{ C mol}^{-1}$, N_A is Avogadro's constant, the number of particles present in one mole of a species, $N_A = 6.02214199 \cdot 10^{23} \text{ mol}^{-1}$.

2.5 Various Forms of Energy

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

2.6 Various Expressions for Work

When work has origins other than those mentioned until now, it is necessary to use appropriate expressions for work in each case.

If the area A of a system, with interfacial tension σ , increases by dA , the work done on the system is:

$$dw = \sigma dA \quad (2.8)$$

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:

$$dw = mg dz \quad (2.9)$$

Lengthening an elastic material by dl under tension \mathcal{T} does work on the system, it is given by:

$$dw = \mathcal{T} dl \quad (2.10)$$

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

$$dw = B dM \quad (2.11)$$

3. First Law of Thermodynamics

3.1 Introduction

Energy exchanges between bodies do occur. One can observe :

- Energy exchange as either work or heat
- Conversion of work to heat or conversely of heat to work
- Energy exchange simultaneously as both work and heat.

The *First Law* formulates some of the rules applicable to energy exchanges. It can be simply stated as : *energy is conserved*.

3.2 The Joule Experiment

By using the fall of a weight in the gravity field of the earth, a paddle wheel that turns in liquid water causes a rise in its temperature. Joule showed that the same temperature rise could be obtained using an electrical resistor heated by an electric current.

Work can be transformed into heat. Heat and work are of the same nature and constitute different forms of energy. They are expressed in the same units.

The joule (symbol J) is the SI unit of energy. 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

The *internal energy* U depends on the state of the system and accounts for all energy exchanges.

We ignore the potential energy of the system in the gravity field of the earth or in external fields.

The internal energy of a system is a state function. The differential of the internal energy U is an exact differential.

3.3.2 Closed System - Adiabatic Process

A *closed system* contained inside an adiabatic enclosure does not exchange heat. When work is done on such a system, it changes its internal energy.

$$q = 0 \quad U_F - U_I = w_{\text{adiabatic}} \quad (3.1)$$

Example

The work done on a gas during an adiabatic process is 1000 J. The change of its internal energy for this process is :

$$U_F - U_I = w_{\text{adiabatic}} = 1000 \text{ J}$$

3.3.3 Closed System - General Process. First Law

Consider a *closed system* exchanging energy with its surroundings as both *work* and *heat*.

Between two given states of the system, the change in the internal energy of the system is independent of the process. This statement actually constitutes the *first law*.

$$U_F - U_I = w + q \quad (3.2)$$

The work done on the system and the heat received by the system depend on the process.

Example

As a result of a thermodynamic process, 1000 J of work is done on a system in contact with a thermal reservoir at 300 K. The system receives -700 J of heat (The system actually transfers heat to the thermal reservoir). The change in the internal energy of the system is :

$$U_F - U_I = w + q = 1000 - 700 = 300 \text{ J}$$

3.3.4 Closed System - Cyclic Process

For a cyclic process, the initial and final states are identical :

$$U_F = U_I \quad \Rightarrow \quad \Delta U = 0 = w + q \quad (3.3)$$

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

3.3.5 Infinitesimal Process

For an infinitesimal process, we can write Eq. 3.2 in a differential form :

$$dU = dw + dq \quad (3.4)$$

dU is an exact differential while, in general, dq and dw are not.

4. Second Law of Thermodynamics

4.1 Kelvin Formulation of the Second Law

The second law of thermodynamics can be formulated in the following way :

Using a system which undergoes a cyclic thermodynamic process, it is impossible to obtain useful work if, globally, heat is only exchanged with one thermal reservoir.

A process where heat is only exchanged with a single thermal reservoir is called a **monothermal process**. Useful work to us corresponds to $w < 0$. In a mathematical form, we can write the Kelvin formulation of the second law as :

$$w \geq 0 \quad \text{cyclic process - single thermal reservoir affected} \quad (4.1)$$

As a consequence, for a *cyclic monothermal process*, we have :

$$\Delta U = w + q = 0 \quad \Rightarrow \quad q \leq 0 \quad (4.2)$$

It can be shown that for a *cyclic monothermal reversible process* $w = 0$.

4.2 Carnot Cycle. Heat Engine. Thermodynamic Temperature

The **Carnot cycle** is a **dithermal reversible cycle**. The system exchanges heat *reversibly* with two thermal reservoirs at temperatures, T_c (cold) and T_h (hot) (see Fig. 4.1).

Due to the reversibility requirements :

- The system can only be brought in contact with a thermal reservoir when its temperature is identical to the temperature of the thermal reservoir. While in contact with the thermal reservoir, the process is *isothermal*, the system temperature is uniform.
- When the system is not in contact with one of the thermal reservoirs, the process that it undergoes *can only be adiabatic*. The system then receives or provides work. Its internal energy changes and so does its temperature.

Therefore, the **Carnot cycle** comprises the following steps :

- 1-2 Isothermal (reversible) process in contact with the thermal reservoir at high temperature T_h , the system receives q_h

- 2-3 Reversible adiabatic process that changes the system temperature from T_h to T_ℓ
- 3-4 Isothermal (reversible) process in contact with the thermal reservoir at low temperature T_ℓ , the system receives q_ℓ
- 4-1 Reversible adiabatic process that changes the system temperature from T_ℓ to T_h .

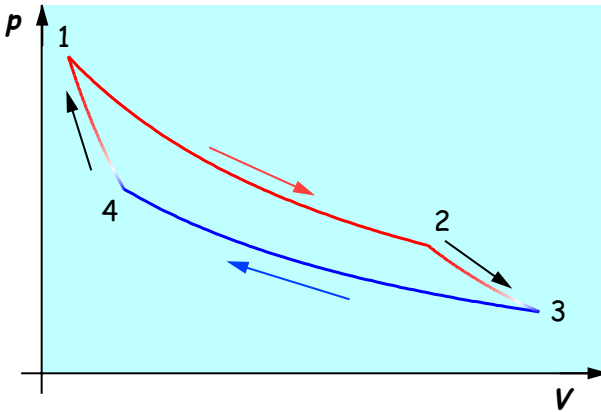


Figure 4.1 Example of a Carnot engine cycle.

An engine provides work to a user (w is negative). For a **Carnot engine cycle** (or **forward Carnot cycle**), it can be shown that we have the following relations:

$$\begin{aligned} w + q_h + q_\ell &= 0 \\ w < 0 \quad q_\ell < 0 \end{aligned} \quad \Rightarrow \quad \left\{ \begin{array}{l} q_h > 0 \\ \text{and } q_h > |q_\ell| \end{array} \right\} \quad (4.3)$$

where w is the algebraic work done on the system during the cycle.

For any system undergoing a *reversible Carnot cycle*, one can show that the ratio of the amount of heat received by a system from each thermal reservoir is independent of the system and depends only on the thermal reservoirs.

This fact is used to define a temperature scale that has a universal character, the **thermodynamic temperature**. We write:

$$\frac{T_h}{T_\ell} = -\frac{q_h}{q_\ell} \quad \Rightarrow \quad \frac{q_h}{T_h} + \frac{q_\ell}{T_\ell} = 0 \quad (4.4)$$

This choice implies that the temperatures of the thermal reservoirs have the same sign on this scale and are always positive. We also have:

$$T_h > T_\ell \quad (4.5)$$

The temperature of the hot thermal reservoir is larger than that of the cold thermal reservoir.

Unique temperature values are obtained by selecting as a reference for the thermodynamic temperature the triple point of water, temperature at which ice, liquid water and water vapor are at equilibrium[†]. The vapor pressure of liquid water is then 6.11 mbar (hPa). The numerical value selected for that temperature is $T_{tp, H_2O} = 273.16$ K, the temperature unit is the kelvin (symbol K). With this choice, the temperature at which ice melts under a pressure of 1 bar is 273.15 K and the boiling temperature of water under the normal pressure of 1 atm is 373.15 K. This selection leads, for these two phenomena, to a difference of 100 K on the thermodynamic scale and a 100°C difference on the Celsius (centigrade) temperature scale.

All the equations of thermodynamics are only valid if we use the thermodynamic temperature scale.

Under the SI standard pressure of 1 bar, the boiling temperature of water is 372.8 K.

Example

As a result of a Carnot cycle, a system provides 1000 J of work. Therefore – 1000 J of work is done on a system that comes in contact with thermal reservoirs at 1500 K and 300 K. This system actually does work on its surroundings. The ratio of the amount of heat received by the system from the thermal reservoirs is :

$$\frac{T_h}{T_\ell} = -\frac{q_h}{q_\ell} \quad \Rightarrow \quad \frac{q_h}{q_\ell} = -\frac{1500}{300} = -5$$

The amounts of heat received by the thermal reservoirs are :

$$w + q_h + q_\ell = 0 \quad \Rightarrow \quad -1000 - 5q_\ell + q_\ell = 0 \quad \Rightarrow \quad \begin{aligned} q_\ell &= -250 \text{ J} \\ q_h &= 1250 \text{ J} \end{aligned}$$

We find that 250 J of energy is “wasted” to obtain 1000 J of work.

4.3 Entropy. Reversible and Irreversible Processes. Equilibrium

4.3.1 Definition

We define a new function called entropy. During an infinitesimal *reversible* change of a system in contact with a thermal reservoir at temperature T , **the entropy of the system** varies by :

$$dS_{\text{sys}} = \frac{dq_{\text{rev}}}{T} \quad (4.6)$$

[†] Phase equilibrium is presented in chapter 8.

dq_{rev} is the amount of heat received by the system during the reversible process. *The entropy S of a system is a state function.* During an **adiabatic reversible process**, the system entropy does not vary since $dq_{\text{rev}} = 0$. An **adiabatic reversible process** is also called an **isentropic process**. Equation 4.4 indicates that as a result of a Carnot cycle, the entropy of the system does not change.

Example

During a reversible adiabatic process, 2500 J of work is done on a system. The internal energy change of the system is :

$$U_F - U_I = w_{\text{adiabatic}} = 2500 \text{ J}$$

The entropy change of the system is :

$$S_F - S_I = 0 \text{ J K}^{-1}$$

4.3.2 The Second Law, Entropy and Spontaneity of Processes

If a closed adiabatic system evolves irreversibly and thus spontaneously, its entropy in its final state is larger than its entropy in its initial state. This statement can be shown to be a direct consequence of the Kelvin formulation given at the beginning of this chapter[†].

$$S_{\text{final}} > S_{\text{initial}} \quad \Leftrightarrow \quad S_{\text{final}} - S_{\text{initial}} > 0 \quad (4.7)$$

Note that any spontaneous process is irreversible. It usually takes place as a consequence of some change imposed to the system or to part of it. Since reversible adiabatic processes are isentropic, we can also state :

It is impossible to imagine a process for a closed adiabatic system that would result in a decrease of its entropy.

Consider now a system that can be in contact with a thermal reservoir at temperature T_{therm} . The *global system* (system of interest plus the thermal reservoir) is an adiabatic system. For an irreversible process, *the entropy change of the global system is positive.*

For any process of a *closed adiabatic global system*, we have the relation :

$$\begin{aligned} \text{global system} &= \text{system of interest plus thermal reservoir} \\ dS_{\text{global}} &\geq 0 \quad (S_F - S_I)_{\text{global}} \geq 0 \end{aligned} \quad (4.8)$$

The equality applies to a *reversible process* and the inequality to an *irreversible one*. It is often possible to consider that a system and its surroundings constitute an adiabatic closed system. The entropy of an adiabatic closed system does not change during a *reversible process*.

[†] The Bases of Chemical Thermodynamics, M. Graetzel & P. Infelta, chapter 4.

Example

Consider a system undergoing a Carnot cycle. For this cyclic process the entropy change of the system is zero since the initial and final states of the system are the same. The entropy changes of the thermal reservoirs are :

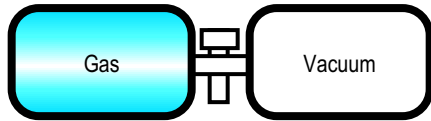
$$(S_F - S_I)_{\text{therm } h} = -\frac{q_h}{T_h} \quad (S_F - S_I)_{\text{therm } \ell} = -\frac{q_\ell}{T_\ell}$$

In virtue of Eq. 4.4, the global entropy change (system plus thermal reservoirs) is found to be zero.

Example

Consider two containers with adiabatic walls separated by a stopcock. Initially, one container contains one mole of an ideal gas at a pressure of 1 bar, while container 2 is evacuated. Both containers have the same volume. The initial temperature of the gas is 25°C.

We open the stopcock. An irreversible expansion takes place and the gas occupies the entire volume at its disposal. Since the system is adiabatic, $q = 0$, and the system volume does not change, $w = 0$, the internal energy of the gas does not change.



$$U_F - U_I = 0 = w + q$$

The internal energy of an ideal gas depends only on its temperature (chapter 7). When the system has reached equilibrium, its temperature has not changed. The change in the entropy of the gas can be obtained starting from (Eq. 4.13) using also the ideal gas law :

$$dU = 0 = -p dV + T dS \Rightarrow dS = \frac{p}{T} dV = nR \frac{dV}{V}$$

$$S_F - S_I = nR \int_{V_I}^{V_F} \frac{dV}{V} = nR \ln \frac{V_F}{V_I} = 8.3145 \cdot \ln 2 \approx 5.76 \text{ J K}^{-1}$$

For this irreversible adiabatic process, the entropy of the system increases.

4.3.3 System in Contact with a Single Thermal Reservoir

Consider a process of a *closed system* that can exchange heat with only one thermal reservoir at temperature T_{therm} during part of the process. The global system (subscript $_{\text{global}}$) made of the system and the thermal reservoir, is a closed adiabatic system. The system receives q_{sys} . The amount of heat received by the thermal reservoir is :

$$q_{\text{therm}} = -q_{\text{sys}} \quad (4.9)$$

Since the global change of entropy cannot be negative, we have :

$$\left. \begin{aligned} (S_F - S_I)_{\text{global}} &= (S_F - S_I)_{\text{sys}} + (S_F - S_I)_{\text{therm}} \\ &= (S_F - S_I)_{\text{sys}} - \frac{q_{\text{sys}}}{T_{\text{therm}}} \geq 0 \end{aligned} \right\} \quad (4.10)$$

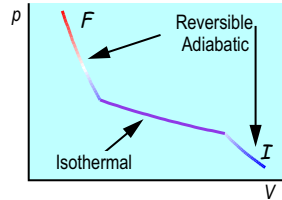
From which we can write :

$$q_{\text{sys}} \leq T_{\text{therm}} (S_F - S_I)_{\text{sys}} = (q_{\text{sys}})_{\text{rev}} \quad (4.11)$$

For a system going from state I to state F , the amount of heat the system receives is smaller for an irreversible process than for a reversible one. The last equality in Eq. 4.11 is justified by imagining a reversible process that takes the system from its initial to its final state. We carry out a reversible adiabatic process to bring the system temperature to T_{therm} , followed by a (reversible) isothermal process at T_{therm} and finally another adiabatic reversible process to bring the system to its final state, thus the expression for $(q_{\text{sys}})_{\text{rev}}$.

Example

Here, we show the reversible path for a gaseous system going from an initial state I to a final state F , via a reversible adiabatic process followed by an isothermal process at the temperature T_{therm} and finally another reversible adiabatic process to bring the system temperature to T_F . The entropy of the system varies only during the isothermal part of the process.



4.3.4 Clausius Inequality

Consider a system that, during a cycle, comes in contact with several thermal reservoirs at different temperatures, $T_1, T_2, \dots, T_i, \dots, T_n$. The entropy change of the system during the cycle is of course zero since entropy is a state function. Using the inequality established in (4.10) for each thermal reservoir and summing for all thermal reservoirs, we can write :

$$\left. \begin{aligned} 0 = \Delta S_{\text{sys}} &= \sum_{i=1}^n \Delta S_{i \text{ sys}} \geq \sum_{i=1}^n \frac{q_{i \text{ sys}}}{T_i} \Rightarrow \sum_{i=1}^n \frac{q_{i \text{ sys}}}{T_i} \leq 0 \\ \text{for a system} & \\ \text{in contact with} & \\ \text{two thermal} & \\ \text{reservoirs} & \quad \frac{q_h}{T_h} + \frac{q_\ell}{T_\ell} \leq 0 \end{aligned} \right\} \quad (4.12)$$

$q_{i \text{ sys}}$ is the amount of heat received by the system from the thermal reservoir at temperature T_i . The equality is valid for a reversible cycle while the inequality applies to any irreversible cycle.

Example

For a cyclic process of a system entering in contact with n thermal reservoirs, the entropy change of the system is zero. From the amount of heat received by the thermal reservoir at temperature T_i , we find the entropy change of that thermal reservoir to be :

$$(S_F - S_I)_{\text{therm } i} = -\frac{q_{i \text{ sys}}}{T_i} \quad \Rightarrow \quad (S_F - S_I)_{\text{global}} = \sum_{i=1}^n -\frac{q_{i \text{ sys}}}{T_i} \geq 0$$

We find using 4.12 that the global entropy change is positive for an irreversible cyclic process and zero for a reversible one.

4.3.5 Differential Expression for the Internal Energy and Enthalpy of a Closed System

Assume that *work due to volume change* is the only type of work done on a closed system (without chemical reactions). For a reversible process, the external pressure is equal to the internal pressure (system pressure) and the system temperature is equal to a thermal reservoir temperature if and when there is thermal contact (needed of course for heat exchange).

$$\left. \begin{aligned} p_{\text{ext}} &= p_{\text{int}} = p \\ dU &= dw + dq_{\text{rev}} = -p_{\text{ext}} dV + T dS = -p dV + T dS \end{aligned} \right\} \quad (4.13)$$

The resulting expression is *valid for any process, even irreversible processes*, since U is a function of state and dU is an exact differential.

Enthalpy is another extensive state function. We can find the expression for the differential of enthalpy from the expression just obtained for dU :

$$H = U + pV \quad \Rightarrow \quad dH = dU + p dV + V dp = T dS + V dp \quad (4.14)$$

Example

Let us find the differential expression for the entropy change of n moles of a pure ideal gas. From the two different expressions of the differential of the internal energy of n moles of an ideal gas, we obtain :

$$dU = n C_{V,m} dT = -p dV + T dS \quad \Rightarrow \quad dS = n \frac{C_{V,m}}{T} dT + \frac{p}{T} dV = n \left(\frac{C_{V,m}}{T} dT + \frac{R}{V} dV \right)$$

$C_{V,m}$ is the molar heat capacity of the gas at constant volume (see chapters 5 and 6). This differential expression can be integrated assuming that the molar heat capacity of the gas

is constant. We obtain the expression for the change in entropy of an ideal gas characterized by its temperature and volume :

$$S_F - S_I = n \left[C_{V,m} \ln \left(\frac{T_F}{T_I} \right) + R \ln \left(\frac{V_F}{V_I} \right) \right]$$

Using the ideal gas law and Eq. 5.52, we find expressions for the entropy change when the states are characterized by other variables :

$$S_F - S_I = n \left[C_{V,m} \ln \left(\frac{p_F V_F}{p_I V_I} \right) + R \ln \left(\frac{V_F}{V_I} \right) \right] = n \left[C_{V,m} \ln \left(\frac{p_F}{p_I} \right) + C_{p,m} \ln \left(\frac{V_F}{V_I} \right) \right]$$

$$S_F - S_I = n \left[C_{V,m} \ln \left(\frac{T_F}{T_I} \right) + R \ln \left(\frac{p_I T_F}{p_F T_I} \right) \right] = n \left[C_{p,m} \ln \left(\frac{T_F}{T_I} \right) - R \ln \left(\frac{p_F}{p_I} \right) \right]$$

$C_{p,m}$ is the molar heat capacity of the gas at constant pressure (chapters 5 and 6).

4.3.6 Equilibrium Condition

Let us now consider a chemical system in an adiabatic enclosure. An irreversible, thus spontaneous, process can take place only if it results in an increase in entropy of the system. Such a process keeps on going until the entropy of the system can no longer increase. The system is then at equilibrium and its entropy has reached a maximum.

When no spontaneous process takes place, the entropy of a closed adiabatic system is maximal and the system is at equilibrium.

4.3.7 Thermal Equilibrium

Consider two identical blocks of matter in thermal contact with each other ($C_{p1} = C_{p2} = C_p =$ Heat capacities of each block at constant pressure). The system is adiabatic. The heat transfer is assumed to be very slow (then the temperature of each block stays uniform). The amount of heat received by a system during an isobaric (constant pressure) process is the change of its *enthalpy* (See § 5.2).

Since the global system receives no heat, the change of its enthalpy is zero. We obtain the final temperature, T_F :

$$\left. \begin{aligned} H_F - H_I &= \int_{T_1}^{T_F} C_p dT + \int_{T_2}^{T_F} C_p dT = C_p (T_F - T_1) + C_p (T_F - T_2) = 0 \\ \Rightarrow T_F &= \frac{T_1 + T_2}{2} \end{aligned} \right\} \quad (4.15)$$

The entropy change of the system during the process is :



Figure 4.2 Heat exchange between two blocks of matter at different temperatures. Globally, the system receives no heat.

$$S_F - S_I = \int_{T_1}^{T_F} \frac{C_p}{T} dT + \int_{T_2}^{T_F} \frac{C_p}{T} dT = C_p \ln \frac{T_F}{T_1} + C_p \ln \frac{T_F}{T_2} \quad (4.16)$$

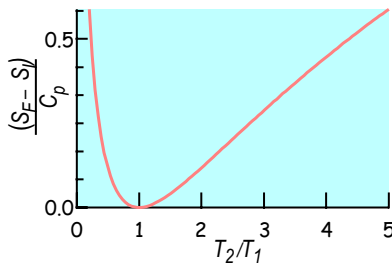
$$\left. \begin{aligned} S_F - S_I &= C_p \ln \frac{T_F^2}{T_1 T_2} = C_p \ln \frac{(T_1 + T_2)^2}{4 T_1 T_2} \\ &\Downarrow \\ S_F - S_I &= C_p \ln \left(1 + \frac{(T_1 - T_2)^2}{4 T_1 T_2} \right) \end{aligned} \right\} \quad (4.17)$$

The entropy change of this closed adiabatic system is always positive, except if both blocks are at the same temperature. Then no process takes place, since the blocks are already in thermal equilibrium.

Example

Let us examine how the ratio $(S_F - S_I)/C_p$ varies with the ratio T_2/T_1 of the initial temperatures of the blocks. We have :

$$\frac{S_F - S_I}{C_p} = \ln \left[1 + \frac{\left(1 - \frac{T_2}{T_1} \right)^2}{4 \frac{T_2}{T_1}} \right]$$



We see that if, in the initial state, the temperatures of the blocks are different, the heat transfer implies an increase of the entropy of the system. A bigger difference in the initial temperatures results in a larger entropy increase.