III. Thermodynamic Phenomenology

The previous section has presented a general idea of the enormous range of behavior that natural systems are capable of, including ***orderly, predictable processes***, in one extreme, and ***random, chaotic processes***, in the other. Thermodynamics describes only one extreme, the chaotic regime. It is important to realize that this latter theory is a consequence of the well-known principles of classical and quantum interactions. There is no fundamental difference between deterministic and statistical behavior. It is the result of research conducted only in the last few decades of the 20th century that has allowed to draw such a consistent picture of nature.

On the other hand, the ***foundations of Thermodynamics*** have been laid early in the last century. This development of a basic theory of random processes has resulted in the still ***modern technology*** of all kinds of thermodynamic engines, from steam and Otto engines to turbofans and rocket engines propelling modern air- and spacecraft. This theory provides also an explanation of why ***chemical and other types of complex reactions*** proceed on average in certain directions and suggests ways in which to influence the course of such reactions. Thermodynamic principles are found at work in large-scale industrial chemical reactors, in the operation of a fast silicon computer chips, as well as in the human metabolism.

III.1. Thermodynamic Systems and State Properties

The objects of study in physical chemistry are called generically ***systems***. As a system, one considers generally an amount of matter enclosed in a ***container***, or in a ***containing field***. The physical properties of the container walls lead to different behavior of the system, because the degree of its communication with the potentially rather different ***surroundings*** depends on the permeability of these walls. System plus surroundings make up the ***Universe***. One distinguishes the following ***system types***:

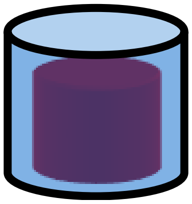

Fig. III-1a: Isolated system. *No mass or heat exchange*

Isolated systems do not interact at all with the surroundings. The container is impermeable to any form of energy or matter, i.e., it has ***adiabatic walls***. Then, the ***total energy E***, the ***number of particles N***, and the ***volume V <u>of the system</u>*** are conserved and well defined. These quantities can be used to characterize the so-called ***macrostate of the system***.

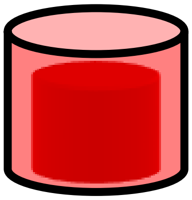

Fig. III-1b: Closed system. *No mass exchange*

Closed systems have walls that are impermeable for particles but permeable for energy. The corresponding containers have ***diathermic walls***. For such systems, only ***particle number*** and ***volume*** are conserved, while energy can be exchanged with the surroundings. The energy can then fluctuate about an ***average value***, which is equivalent to the ***temperature*** of the system. A macrostate is characterized by ***T, N,*** and ***V***.

Open systems can exchange both energy and particles with the surroundings. In equilibrium with its surroundings, an open system's ***average values*** of total energy and of particle number are

Fig. III-1c:
Open system. *Mass and heat exchange*

determined by the ambient temperature and the ***chemical potential*** μ, respectively. A macrostate is characterized by T and μ.

If the properties of a system are identical for any subpart of it, the system is called ***homogeneous***. If these properties change suddenly at interfaces, the system is ***heterogeneous***. The homogenous parts of such a system are its ***phases***, the separating surfaces are the phase boundaries. In the example of a closed pot with water, vapor, and air, the phase boundary is the water surface, the water is the ***liquid phase***, the vapor/air ***mixture*** is the ***gas phase***.

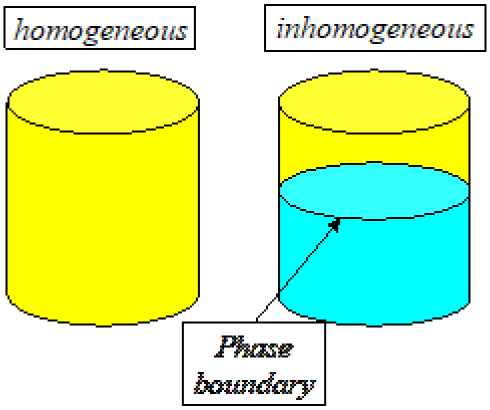

Figure III-2

The macroscopic variables describing the state of the system, the ***state variables***, can depend in a different fashion on the ***size of the system***:

- ***Extensive (additive) state variables scale*** in proportion to the mass of the system, or its number of particles. Typical extensive variables are volume and total energy. For a heterogeneous system, the state variables for its component phases simply add.

- ***Intensive state variables do not scale*** with the size of the system. Examples are pressure, temperature, refractive index, etc. Intensive variables can be defined locally, they may vary spatially, such as density or pressure of the atmosphere.

The table below summarizes the units of the most common observables of interest.

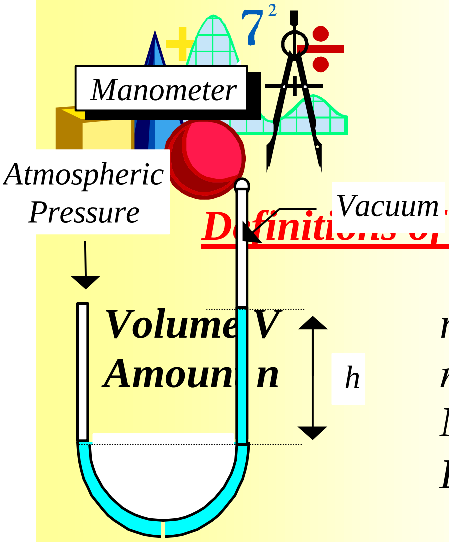

Figure III-3

Definitions of Units (Système International):

Volume V	m^3
Amount n	number of moles (Avogadro's Number: $L = 6.022 \bullet 10^{23}$ particles /mole)
Pressure p (P)	1 Pa (Pascal) = 1 Nm^{-2} = 1 kg $m^{-1}s^{-2}$ 1 bar = 10^5 Pa ≈ 1 atm 1 atm = 101 325 Pa=760 Torr≈ 760 mm Hg
Standard Pressure	p_0 = 1 bar ≈ 1 atm
Temperature T	1 K (Kelvin); T([K])= T([°C]) + 273.15 K Celsius scale defined by freezing point (T=0 °C) and boiling point (T=100 °C) of water.

Standard temperature T_0 = 298.15 K (25 °C)

To measure the state properties is not always trivial. The pressure measurement is, however, straight forward, using barometers or a manometer such as illustrated in the sketch. Here, two communicating glass tubes of cross section area *A* are filled with some kind of a non-volatile liquid. One tube is closed at the end and evacuated, the other is open to the atmosphere. One observes that the height of the liquid columns is different in the two tubes.

This is expected, because the atmospheric pressure *p* works only on the surface of the liquid exposed to the atmosphere, and there is no counter pressure from the evacuated part of the other tube. Consequently, the force $\boldsymbol{F = p \bullet A}$, associated with the atmospheric pressure forces the liquid up into the evacuated tube, but only up to a certain height *h* above the reference level of the liquid in the open tube, corresponding to an excess volume $\boldsymbol{V = A \bullet h}$. At this height, the ***force due to the atmospheric pressure on the surface of the liquid in the open tube is exactly balanced by the weight mg of the excess liquid*** in the evacuated column. With a liquid density of $\boldsymbol{\rho}$ and a gravitational acceleration $\boldsymbol{g}$, one calculates

$$F = p \bullet A = m \bullet g = \rho \bullet V \bullet g = (\rho \bullet A \bullet g) \bullet h \tag{III.48}$$

i.e.,

$$p = (\rho \bullet g) \bullet h \propto h \tag{III.49}$$

Therefore, in the above manometer, one has a ***linear pressure gauge***. The particular geometry was chosen to make the quantitative consideration most obvious. However, the two connected tubes do not have to have the same diameter for the manometer to work.

There are also well-known physical effects that indicate a ***sensitive response of matter to heating*** up. For example, a metal rod is shorter at freezing temperature than at the temperature of boiling water, and the relation between length of the rod and temperature is monotonic and even linear. The volumes of gases at low pressures also show sensitivity to the temperature, which can be used to measure the latter.

Nevertheless, the measurement of a ***temperature*** is not as straight-forward as the measurement of a pressure. The former invokes an important principle, known under the name of

The Zeroth Law of Thermodynamics

Here, two different systems are said to be in ***thermal equilibrium***, if they have the same temperature *T*, if they are ***"equally hot"***.

This law is purely phenomenological: One knows from experience that, if one brings two pieces of matter into close mechanical contact, they will eventually become equally hot. This is achieved by a cooling of the hotter and a heating of the cooler piece. For example, ***mixing*** equal amounts of boiling ($T = T_1$) and freezing water ($T = T_2$) produces, after some short time, water at an ***intermediate temperature*** ($T = [T_1 + T_2]/2$).

If two systems A and B are in thermal equilibrium with a third system, C, then A and B are in equilibrium with each other. (II.50)

So, then, one could use a metal rod, dip it into water at a defined temperature and calibrate its length. One finds a linear law for the expansion of the rod of initial length $l(T_1)$ at temperature T_1:

$$l(T) = l(T_1)\cdot\ 1 + \beta\cdot(T - T_1) \qquad \text{(III.51)}$$

where β is the (*linear*) ***thermal expansion coefficient*** of the particular metal.

Similarly, the French chemist ***Gay-Lussac*** (1778-1850) found a linear relationship between the volume *V* of ***very dilute*** ($p \approx 0$), or ***ideal***, gases and the temperature:

$$V(T) = V_0 \bullet (1 + \alpha \bullet T) \qquad \text{(III.52)}$$

where V_0 is the volume at $T = 0\,°C$.

A very surprising result of his studies was that ***all such "ideal" gases had the same cubic expansion coefficient*** of

$$\alpha = T_0^{-1} = [273.15\,°C]^{-1}$$

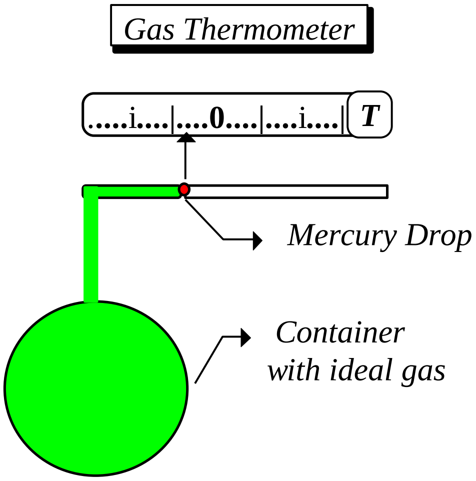

Figure III-4

(The slopes of the straight lines in the sketch on the left are given by the different quantities $V_0 \bullet \alpha$. They differ only if different volumes V_0 are taken for the different gases). All lines intercepted the abscissa ($V = 0$) at the same temperature:

$$T_0 = -273.15\,°C \qquad \text{(III.53)}$$

Since there are no negative volumes, this temperature had to represent ***"the absolute zero"***. Of course, the measurements had to stop, before *liquefaction* of the gases set in. This observation suggested to introduce a new temperature scale, the ***Kelvin scale***, whose zero was identical with the above value of T_0. With a temperature defined on this Kelvin scale, i.e., replacing $T\delta(T-T_0)$ in Equ. III.52, one obtains a simpler scaling law for the gas volume with T,

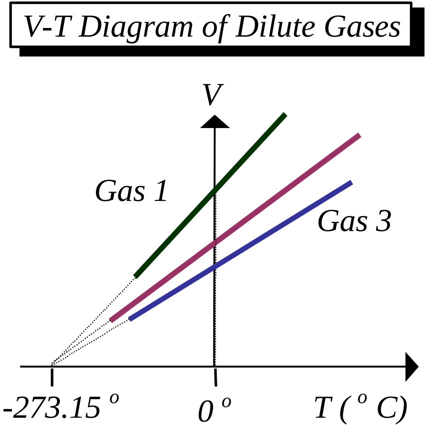

Figure III-5

$$V(T) = \alpha' \bullet T \qquad \text{(III.54)}$$

which is completely equivalent to the law of Equ. III.52. Thus, by choosing a standard temperature of T_0 (e.g., that of the freezing point of water), one can calibrate an ***ideal-gas thermometer*** such as shown in the sketch. Then, one determines the ratio, T/T_0, of prevailing temperature T to standard temperature T_0 from the measured volume ratio

$$V(T) = V(T_0) \bullet (T/T_0) \qquad \text{(III.55)}$$

according to Equ. III.54.

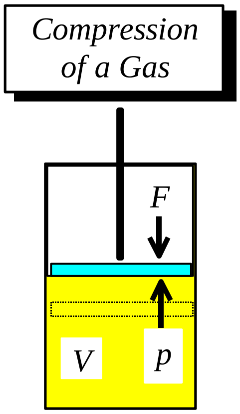

Figure III-5

Another, very important, empirical gas law is named, after the English chemist ***Robert Boyle***, ***Boyle's Law***. He found that, for a given amount of gas and a fixed temperature, the ***internal gas pressure p increased when the gas was compressed by the action of an external force F***, i.e., when the gas volume V was decreased, and *vice versa*. This was evident from the fact that the external force F, that had to be applied to affect the compression and balanced the internal pressure p, had to be raised (see sketch). The experimental correlation $p(V)$ was well described by a ***hyperbolic function***

$$p(V) \propto 1/V \qquad \text{(III.56)}$$

Varying the temperature, Boyle and his contemporaries observed that it was more difficult to compress a gas at higher temperature T than at lower value of T. Combining these observations, one has ***Boyle's Law:***

$$p \bullet V = const.(T, n) \qquad \text{(III.57)}$$

It states that, for a given amount *n* (number of moles) of an ideal gas and at a given temperature *T*, the product of (internal) pressure and volume of a gas stays constant. Specifically, the steepness of the curve *p(V)* is directly proportional to *T*,

$$p \cdot V = const.(n) \bullet T \qquad \text{(III.58)}$$

with a constant that depends only on the number *n* of moles in the gas volume. This behavior is a reflection of the law by ***Gay-Lussac*** (Equ. III.54).