Preface: A Question of Thermodynamics

It is a well-known fact that any thermodynamic system consists of a very large number of particles... so large that to count the molecules in a 1-g drop of water, at a rate of 100 molecules per second, you would need 10,000 billion years! A child celebrating his birthday and blowing out the candles at a rate of 1,000 molecules of air per second would take some 400 billion years to expel 0.5 L of air. ...

These particles are in uninterrupted motion so the air molecules you have around you, in a "static" situation at about 18 °C, have an average *translational fluctuation velocity* of about 500 m/s... or 1,800 km/h!

Three degrees of freedom are associated with the translation movement of a particle in three-dimensional space.

The average density of the kinetic energy of translational fluctuation per mole can be adopted as the basis of the true thermodynamic temperature—let's call it θ! It is expressed in J/mol. While the conventional measure of temperature T, for historical reasons, was based on a sensorial approach and expressed in °C, °F, or K, the true thermodynamic temperature is a physical concept which correlates with T (in K) through $\theta = 3/2\,RT$. This is very important and it makes much more sense to let our students, researchers, and engineers think of temperature in terms of J/mol instead of °C... given that 12.5 J/mol represents approximately 1 K.

T (°C)	−273	−193	−113	−33	−18	0	20	37	42	100
T (K)	0	80	160	241	255	273	293	310	315	373
θ (J/mol)	0	1,000	2,000	3,000	3,182	3,406	3,656	3,868	3,930	4,652

This translational fluctuation velocity is not uniform for all particles and a "normal" distribution allows the highest translational fluctuation energy particles in a liquid to fly (evaporate) from the surface to the surrounding atmosphere. The higher the average translational fluctuation energy, the greater the number of particles flying off. In other words, the higher the temperature of a liquid, the higher the vapor pressure.

When the energy brought by "evaporation" (flying particles) is supplied by the system itself, the operation is called "autovaporization"; (It is like a family paying

for a flight for one of its members; the flight can be financed using the family's own capital, it is self-financed).

The study of industrial unit operations inevitably requires a fundamental analysis of thermodynamic transformations, various mass and heat transfers, chemical and enzymatic reactions, mechanical/rheological behavior and characteristics. Studies have been carried out on a large number of transfer phenomena that occur between or inside media. Here, change over time reveals the exchange processes in quasi-static systems: the homogeneous isotropic translation movement of particles in different amounts and in different zones establishes gradients of temperature and concentration which act as driving forces.

Some operations involve *transitory periods* which are so short that they are generally considered to be negligible. However, the impact of such transitory periods has been proved to be so effective that it is essential that they would be the subject of specific studies. During the very short period when the pressure is dropped abruptly, the initial isotropic translational fluctuation velocity ceases being random in one of the three dimensions; then two dimensions of the initial three dimensional-translational fluctuation velocity define the temperature, whose value, from an asymptotic point of view, becomes $\theta_m = 2/3 \ \theta_i$. This modification of temperature is achieved without an exchange of energy with the external medium and does not respect the conventional quasi-static transfer laws. When this can achieve autovaporization at the industrial level, the particular impact is to produce higher yields thanks to a fall in temperature, which widely overshoots the equilibrium level. This can be considered as the basis for improving industrial operation performances in terms of energy consumption and environment features.

Thermodynamics then has two asymptotic limits: the quasi-static field, which concerns long transformations; and the very short and specific instantaneous field. Instant controlled pressure drop (DIC) belongs to the latter field in one of the technological applications described in this book.

Other transitory-type processes have been considered as innovative approaches in the intensification of industrial unit operations. The main concerns in this field have been the possibility of using such transitory stages of thermodynamic transformations to establish much more effective mass transfers. Using the total pressure gradient as a driving force instead of the vapor pressure of a standard diffusion transfer (Fick-type transfer) allows us to define the instant auto-vaporization which can markedly improve drying and essential oil extraction.

Temperature, Definition, and Presentation

Temperature is now well defined: it is the density of the kinetic energy of the translational fluctuation motion of the particles in a system. Thus it is possible to define the term "temperature" as a physical quantity according to the relationship

between the thermodynamic-temperature θ and the density of the kinetic energy per mole for the translational fluctuation of particles in a system:

$$\theta = \frac{3}{2}RT = \frac{1}{2}MV_t^2 \tag{1}$$

where θ is the quantity reflecting the system temperature (J mol^{-1}); R is a constant called the universal ideal gas constant ($R = 8.314$ J mol^{-1} K^{-1}); T is the temperature expressed in Kelvin K; M is the molar mass of the particles forming the system being studied; V_t is the mean translational velocity of the particles; it is a random 3-dimensional isotropic velocity with a statistically homogeneous value $V_t^2 = V_x^2 + V_y^2 + V_z^2 = 3V_x^2$.

Whatever the size and the composition, a system is mainly characterized by an extremely large number of huge and randomly moving particles. The total velocity of the system derived from each particle can be defined as follows.

Total velocity:

$$\vec{v}_G = \frac{\sum m_i \vec{v}_i}{\sum m_i} = \frac{\sum m_i \vec{v}_i}{m} \tag{2}$$

When the total velocity $\vec{v}_G$ is nil, the system is static, although $\vec{v}_i \neq 0$.

When the composition of these different velocities leads to a total velocity that is different from zero, the system has an apparent motion which has to be added to the internal fluctuating velocities.

Absolute and relative velocities:

$$\vec{v}_i = \vec{v}_G + \vec{V}_i \tag{3}$$

where $\vec{v}_i$ is the absolute (laboratory frame) velocity of the particle i; $\vec{v}_G$ is the absolute (laboratory frame) total velocity (of the center of mass) of the system; $m = \sum m_i$ is the mass of the system, which is the sum of the masses of each particle; $\vec{V}_i$ is the relative (center of mass frame) velocity of the particle i. Its average value rapidly leads to a homogeneous distribution of particles and particle velocities in the system which becomes 3-D isotropic and statistically homogeneous.

Thus, the integral kinetic energy of the system is due to the two components of velocity: macroscopic (displacement of the center of mass, with the general external kinetic energy) and random (internal kinetic energy of fluctuation, not necessarily limited to the translational motion).

Integral kinetic energy E_k of a system:

$$E_k = \sum \frac{1}{2} m_i v_i^2 = \frac{1}{2} m v_G^2 + \sum \frac{1}{2} m_i V_i^2 \tag{4}$$

The translational part of internal kinetic energy of fluctuation $\sum \frac{1}{2} m_i V_i^2$ is linked to 3 as degrees of freedom (DoF).

The translational part of the kinetic energy of fluctuation:

$$\sum_{j=1}^{3} \sum \frac{1}{2} m_i V_{t,j,i}^2 = \frac{1}{2} m V_t^2 \tag{5}$$

Other possible motions (vibration, rotation) constitute a complementary degree of freedom. By assuming δ is the total degrees of freedom, the total internal kinetic energy of fluctuation is as follows.

Total internal kinetic energy of fluctuation:

$$E_{k,f} = \sum \frac{1}{2} m_i V_i^2 = \delta \frac{1}{2} m V_{x1}^2 = \frac{\delta}{3} \left(\frac{1}{2} m V_t^2 \right) \tag{6}$$

The integral kinetic energy E_k is the sum of the total external kinetic energy $E_{k,G} = \frac{1}{2} m v_{CM}^2$ and the total internal kinetic energy of fluctuation $\frac{\delta}{3} \left(\frac{1}{2} m V_t^2 \right)$:

$$E_k = E_{k,G} + E_{k,f} = \frac{1}{2} m v_G^2 + \frac{\delta}{3} \left(\frac{1}{2} m V_t^2 \right) \tag{7}$$

This is the situation of a static system (free of interference from the external environment) or a system with quasi-static transformations. The study of thermodynamic systems is an essential element in the analysis of physical, chemical, and biological phenomena.

Once it is isolated, or during quasi-static transformations, the system can have the density of the translational kinetic energy of fluctuation, which is usually three dimensional. It is hence possible to define the term "temperature" as a physical quantity according to the relationship shown in (1).

Before it was defined as a physical quantity, temperature was indicated using "thermometers." This is to link the temperature with physical impacts (dilation, thermoelectricity).

In the case of fluids, the large number of particles and the random translational velocity define the *pressure* as the parameter that is closely coupled to the rate of momentum transferred to the unit area of the wall that defines the system.

Thermodynamic Parameters

A thermodynamic system is defined by its internal energy U. This is the sum of the internal kinetic energy of fluctuation:

$$E_{k,f} = \sum \frac{1}{2} m_i V_i^2 = \frac{\delta}{3} \left(\frac{1}{2} m V_t^2 \right)$$

and the internal (interaction between particles) potential energy

$$E_{p,\text{interaction}} = \sum_{i=1}^{n} \sum_{j \neq i}^{n} E_{p,(i-j)}$$

The internal energy U is the sum of the internal kinetic energy of fluctuation and the potential interaction energy.

$$U = E_{k,f} + E_{p,\text{interaction}} = \frac{\delta}{3} \left(\frac{1}{2} m V_t^2 \right) + \sum_{i=1}^{n} \sum_{j \neq i}^{n} E_{p,(i-j)} \qquad (8)$$

The apparent mechanical energy E_{app} of a system is the sum of the apparent kinetic energy $E_{k,G} = \frac{1}{2} m v_G^2$ and the apparent potential energy $E_{p,G}$:

$$E_{\text{app}} = E_{k,G} + E_{p,G} = \frac{1}{2} m v_G^2 + E_{p,G} \qquad (9)$$

The total energy E of the system is the sum of the apparent mechanical energy E (apparent kinetic energy $E_{k,G} = \frac{1}{2} m v_G^2$ and the apparent potential energy E_p) and the internal energy U. The total energy of the system E is as follows.

$$E = E_{\text{app}} + U \qquad (10)$$

The external medium can supply energy to the system thus modifying its total energy E. The amount supplied can be positive or negative, with organized or fluctuation work. The former comes from the work done by macroscopically moving forces; it is called organized energy work or W.

The second is usually the work done by forces acquiring random movements, i.e., with low and aleatory displacements; it also derives from the fluctuation energy produced by the shocks between external and internal particles and be called fluctuation energy or heat Q.

Energy conservation law:

$$\Delta E = \Delta \left(E_{\text{app}} + U \right) = Q + W \qquad (11)$$

In other words, this expression reflects the first law of thermodynamics (law of conservation of energy).

An isolated thermodynamic system is described as a system where there is no fluctuation energy or heat exchange (Q) with the external environment. The changes in the system are then adiabatic.

Thermodynamic Balance and Quasi-Static Transformations

A system reaches its thermodynamic equilibrium once it attains the different thermal, mechanical, and chemical balances. Thermodynamic equilibrium is determined through thermodynamic potential as the Helmholtz free energy at a constant temperature and volume or the Gibbs free energy for the system at a constant pressure and temperature.

The transformation of a system can sometimes occur too quickly and the particles in a system reach the level of a completely random, isotropic, homogeneous fluctuation velocity. This is then called "non quasi-static transformation." In contrast, a system follows the so-called quasi-static transformation when the change over time of the system, and a possible interaction with the external environment, allows the identification of its thermodynamic parameters at any given moment of the transformation. It is then possible to define the infinitesimal changes throughout the entire transformation.

Direction of Change: Achievable and Unfeasible Transformations

A system that is completely isolated from the external medium tends towards its intrinsic thermodynamic equilibrium. A system interacting with the external environment generally tends towards the thermodynamic equilibrium of both the system and the external medium.

No change is possible without respecting energy conservation; this is called "the first law of thermodynamics."

Not all transformations that respect the first law of thermodynamics are possible; only certain directions of transformation are feasible.

Thus, a system that is completely isolated from the outside with an initial absence of homogeneity in terms of concentration must inevitably tend towards thermodynamic equilibrium, resulting in a homogeneous composition. Inside an isolated system, an inverse trend that increases the concentration gradient is not spontaneously possible. A similar situation is observed in terms of temperature: a system that is initially nonhomogeneous in terms of temperature and is perfectly isolated from the external environment must inevitably tend towards thermodynamic equilibrium, i.e., where there is the same temperature at any point in the system. The inverse tendency is not (spontaneously) possible.

Two systems exchanging fluctuation energy (heat) allow a transformation to occur spontaneously (without external energy) when the transfer is achieved from the body at the highest temperature to the body at the lowest temperature. Transformation between two systems that allows the transfer of organized energy (work W) to full fluctuation energy (heat) can be achieved regardless of the temperature of the systems. However, the inverse operation, where fluctuation energy (heat) passes into organized energy (work) is only partially possible: it requires the transfer of a certain amount of this fluctuation energy to a colder (lower temperature) system.

It was found that the change in a completely isolated system is one that increases its "disorder." When the system is interacting with the external environment, the disorder of the system or the external environment can decrease but a transformation is "feasible" only when it generates a higher total disorder of the Universe, which includes the system and the external environment. The variation in the disorder of a system is defined as being proportional to the ratio between the fluctuation energy (heat) absorbed by a system during a quasi-static transformation and the density of kinetic energy of fluctuation of the particles in the system.

Variation of disorder in the system:

$$\frac{\text{Fluctuation energy (heat) absorbed through quasistatic transformation}}{\text{Density of translational energy fluctuations}} \quad (12)$$

At the microscopic level, the disorder of the system is related to the increase in the probability that the molecules occupy different positions. Disorder can be "measured" by a state function called entropy S. The entropy used in thermodynamics is therefore defined as follows.

Definition of entropy:

$$\mathrm{d}S = \frac{\delta Q}{T} \quad (13)$$

Thus, while the conservation of energy is the first law of thermodynamics, the second law governs the transformations: Any real transformation occurs systematically with an increasing overall disorder (system + external environment); the degree of disorder is measured by the increase in entropy. It can be stated that every real transformation has resulted in the creation of the entropy of the entire universe.

The expression of the second law formalizes the creation of entropy.

A transformation is achievable when total entropy increases:

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{Exterior}} > 0 \quad (14)$$

Increasing disorder, or increase in the total entropy of the universe over time, is an example of what is called the "arrow of time."

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