ENTROPY

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Entropy is important for two main reasons:

- Entropy is a basic concept in physics and information science, being the basic measure to compare different states of an isolated system (the information content of a description). Entropy is the basic thermodynamic variable that serves to define and relate most thermal properties of matter, and the equilibrium state (for an isolated system, the one with maximum entropy, what is known as the Second Law of thermodynamics).
- Entropy is involved in the computation of maximum and actual efficiencies on most useful engineering processes, what serves to categorise the goodness of realisations, and pinpoint where enhancements can be more profitable

Entropy concept

We have seen before that energy is a scalar magnitude of the state of a system that is conservative for isolated systems, which we may visualise as an integral function associated to the motions and positions of its microscopic particles, and that we can easily measure macroscopically as the adiabatic work transfer between two states.

Now we intend to introduce a state variable that measures the distribution of energy and other magnitudes inside the system. The aim is not to measure *any* distribution but to characterise the *most probable* distribution, i.e. the distribution to be expected after an isolated system has had time to loose its initial-state information (due to the practical impossibility to totally avoid the interaction between the system and its surroundings). The statistical variable introduced to measure the distribution is named entropy, *S*, still not a common term to the general public but a scientific-jargon concept for the initiated; the author often gives the following explanation when asked by a lay person:

- Entropy is a measure of the uncertainty on the state of things (the reason why everybody should bet at 7 in the two-dice game), a measure of how energy and other extensive quantities distribute within available constraints in a thermodynamic system. And so on, depending on the feedback obtained:
- We lack an intuitive quantification of entropy (in comparison with energy being related to the speed and height of a mass), but we all have a qualitative feeling of entropy: everything tends to get dispersed, all motion tends to die out, all objects tend to thermalise... Furthermore, there is more empirical evidence on the fact that energy tends to spread out, than on the fact that energy is conservative.
- Entropy (think as dispersion), tends to a maximum within applied constraints. Sometimes, maximum entropy yields 'a uniform distribution' (e.g. density and composition in room air), but most often not (e.g. density and composition in a gravity field).
- By the way, entropy is the reason why oxygen in the air, which is heavier than nitrogen, does not fall to the ground (the tendency to fall is outweighed with the tendency to disperse).
- Entropy measurement in Thermodynamics is nearly as simple as energy measurement: energy in a control-mass system increases when work or heat is added (thing on a piston-cylinder system with trapped air, and how work and heat can be measured); system entropy does not change when work is added 'smoothly', and it increases in the amount $dS=dQ/T$ when heat is added 'smoothly', T being absolute temperature (whose zero is unattainable).

Equilibrium

It is a fact of Nature (known as Second Law of Thermodynamics) that an isolated system, no matter how its magnitudes are initially distributed inside (its density, velocity or energy fields), evolves towards a unique state of minimum bias, called the equilibrium state, in which the averaged uncertainty of the distribution, i.e. its entropy, takes a maximum value. Notice the change in perspective from 'causal' laws describing the change caused by a force, as in Newton's Mechanics, $\vec{F}=m\vec{a}$, to 'teleological' laws describing the purpose of the change: here, to maximise the entropy of isolated systems (in Hamilton's Mechanics, to minimise the action; in Optics, to minimise the time of travel).

However simple the above statement of the Second Law appears (in terms of maximum entropy), the most common statement is based on heat engines (to be explained in the next chapter: Exergy), stating that it is not possible to cyclically generate work from a single heat source (Kelvin-1851); another widely cited statement is based on heat flow: it is not possible to transfer heat from a cold body to a hot body without any changes in the environment (Clausius-1854).

The time to reach equilibrium, i.e. the relaxation time, will be proportional to the size of the system because the forces are mainly local (molecular interaction), thus, for every user-selected time interval, small enough subsystems have already reached its equilibrium state (maximum entropy). Thermodynamic equilibrium requires complete equilibrium, i.e.:

- Mechanical equilibrium, i.e. no accelerations, and thus $\vec{F}_{\text{net}} \equiv \sum \vec{F}_i = 0$ and $\vec{M}_{\text{net}} \equiv \sum \vec{r}_i \times \vec{F}_i = 0$.
- Thermal equilibrium, i.e. no heat transfer, and thus uniform temperature.
- Chemical equilibrium, i.e. no mass diffusion or reactions.

The above-mentioned concept of entropy as the averaged uncertainty of a distribution, was stated in 1948 by the mathematician C. Shannon working at Bell Labs on Information Theory, trying to measure uncertainty, but the name *entropy* was coined in 1865 by the thermodynamicist R. Clausius for the integral of the heat input divided by temperature along a reversible process in a thermal system, based on the concept he introduced in 1850 to measure 'what changes, after everything recovers, after a cycle'. Already in 1877, L. Boltzmann showed that entropy, S, was proportional to the number of equally-probable microscopic states, Ω, in the way $S=k\ln\Omega$, so that the equilibrium state is the one with most chances (really he said proportional to the statistic weight of possible states; states can only be numbered with quantum theory, and, only if states can be numbered, can absolute entropy be defined). In the 1930s, A. Eddington labelled entropy as 'the arrow of time' and linked it to the expansion of the Universe, quantified by E. Hubble in 1929; notice that, before the Theory of Heat, by Fourier in 1822, theoretical Physics was time-reversible (i.e. time-symmetric; e.g. $F=m\mathrm{d}^2x/\mathrm{d}t^2$ is the same for time-advance than for time-reversal). This contradiction (of particle mechanics being time-symmetric whereas Thermodynamics showing a unique direction in time) is known as Loschmidt's paradox.

We intend now to obtain the Clausius result starting from the more general and intuitive concept of Shannon, but many other authors prefer the original approach of introducing entropy from the behaviour of heat engines, one of the key applications of Thermodynamics (see Chap. 3: Exergy). Furthermore, instead of focusing on thermodynamic functions: Energy, Entropy, Exergy…, many books present Thermodynamics as a sequence of Principles: Zeroth Law (thermometry), First Law (calorimetry, basically), Second Law (heat engines, basically), and Third Law (thermochemistry).

The method of partitions release

Consider a partition or distribution of extensive variables in an isolated system; it may range from a two-part hot and cold partition, to the intermediate partition with many subsystems as sketched in Fig. 2.1, to the extreme consideration of a single distinguishable quantum state (identified by its quantum numbers). The distribution is characterised by the amounts of extensive magnitudes belonging to each subsystem. Let $P=\{p_1,p_2,...p_n\}$, with $p_i\geq 0$ and $\Sigma p_i=1$, be a probability distribution function, such that p_i is the probability that the isolated system is found in state i, amongst all the possible states compatible with the fact that the system is isolated and thus its mass, volume, linear momentum, angular momentum, and energy, remain unchanged. If we call uncertainty of the microstate i to $-\ln p_i$, then the average uncertainty for the distribution considered is $-\Sigma p_i \ln p_i$, were the sum extends to all possible states i compatible with the restrictions. Modified with a scalar factor, this average uncertainty is named the (Shannon) entropy of the system:

$$S \equiv -k\sum p_i \ln p_i \qquad (2.1)$$

where k is the Boltzmann constant $k=1.38\cdot 10^{-23}$ J/K in Thermodynamics (in Information Theory, $k=1/\ln 2$ bit, or $k=1$ nat, are chosen, instead; a nat is the natural unit for information entropy, based on natural logarithms and powers of e, rather than the powers of 2 and base 2 logarithms which define the bit). When in 1961 M. Tribus asked Shannon about the genesis of (2.1), the latter answer (quoted by Tribus in Sci. Am. 1971, p. 180): “My greatest concern was about what to call it. I thought of calling it ‘information’ but

the word was overly used, so I decided to call it 'uncertainty'. When I discussed it with John von Neumann, he had a better idea. Von Neumann told me: "You should call it entropy, for two reasons. In the first place, your uncertainty function has been used in statistical mechanics under that name, so it already has a name. In the second place, and more important, no on knows what entropy really is, so in a debate you will always have the advantage.""

Note that compound probabilities are multiplicative, uncertainties are additive and so is entropy. For equally-probable microstates totalising a number Ω, their probability is $p_i=1/\Omega$ and (1) yields Boltzmann's entropy. Notice, by the way, that if there were just one possible state for the system (the fundamental quantum state, with minimum thermal energy, at $T=0$), entropy would be zero, what is known as Nernst theorem (1911) or Third Law of Thermodynamics.

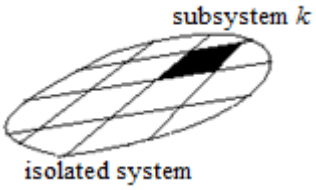

Fig. 2.1. A partition in small control masses m_k of an isolated system of mass m.

Notice that we should only call 'thermodynamic equilibrium' to a state of maximum entropy in a system, i.e. where $dS/dt=0$ with $dS_{univ}/dt=0$, and not to steady states of the system, where $dS/dt=0$ but $dS_{univ}/dt>0$. To check that a stationary system is at equilibrium, one should isolate the system and verify that there is no evolution. Equilibrium does not mean total absence of motion; macroscopic equilibrium corresponds to a dynamic equilibrium at microscopic level (e.g., the same amount of substance vaporising and condensing in a liquid-vapour equilibrium).

Consequences of equilibrium

We cannot find Ω or the p_i in a generic physical system because of its overwhelming complexity; what we want to know is the implication of the entropy being maximum in the state of equilibrium, upon the distribution of mass, energy, and so on. To do that, consider the partition sketched in Fig. 2.1, corresponding to the distribution of energy and volume of small control masses in a single component isolated system, in absence of internal motions and of any external force field so that the energy of the system is just its internal energy U. A generic subsystem k has a constant mass m_k as chosen, but we want to know what energy U_k and volume V_k will correspond to it in the state of equilibrium. The mathematical formulation is:

$$S \equiv \sum S_k = \text{maximum}, \quad U \equiv \sum U_k = \text{constant}, \quad V \equiv \sum V_k = \text{constant} \qquad (2.2)$$

The solution is obtained by the method of Lagrange multipliers, i.e. maximising without restrictions the combined function $\Phi \equiv S+\alpha U+\beta V$, with α and β constants, with respect to the independent variables U_k and V_k, what yields:

$$\Phi \equiv S + \alpha U + \beta V = \sum S_k(U_k, V_k) + \alpha \sum U_k + \beta \sum V_k = \text{maximum}$$

$$\Rightarrow \left\{ \begin{array}{l} \dfrac{\partial \Phi}{\partial U_k} = \dfrac{\partial \mathcal{S}}{\partial U_k} + \alpha \dfrac{\partial U}{\partial U_k} = \dfrac{\partial \mathcal{S}_k}{\partial U_k} + \alpha = 0 \\ \dfrac{\partial \Phi}{\partial V_k} = \dfrac{\partial \mathcal{S}}{\partial V_k} + \beta \dfrac{\partial V}{\partial V_k} = \dfrac{\partial \mathcal{S}_k}{\partial V_k} + \beta = 0 \end{array} \right\} \forall k \qquad (2.3)$$

what means that the equilibrium state is characterised by the fact that $\partial S_k/\partial U_k$=constant and $\partial S_k/\partial V_k$=constant, i.e. the sensitivities of entropy with respect to changes in energy or volume are the same at every conceivable subsystem of a system at equilibrium. It is reasonable (to be checked), a fortiori, to relate these sensitivities to the traditional ideas of temperature and pressure by:

$$\frac{1}{T} \equiv \left. \frac{\partial \mathcal{S}}{\partial U} \right|_V, \quad \frac{p}{T} \equiv \left. \frac{\partial \mathcal{S}}{\partial V} \right|_U \qquad (2.4)$$

Notice, by the way, that temperature and pressure so defined cannot have negative values, since the system would naturally collapse or disintegrate otherwise (e.g. its kinetic energy would diverge if the total energy is constant and the internal energy decreases with entropy). In spite of that, restricted partial systems with finite number of states could be defined, resulting in negative temperatures (hotter than positive ones). Negative pressures, however can be found in practice in some metastables systems (e.g. Natterer's tube experiment).

Proceeding in a similar manner, one may consider the distribution of linear momentum, $m_k \vec{v}_k$, imposing the conservation of total energy $E = \sum \left(U_k + \tfrac{1}{2} m_k \vec{v}_k^2 \right)$, total linear momentum $\vec{P} \equiv \sum m_k \vec{v}_k$, and total angular momentum, $\vec{L} \equiv \sum \vec{r}_k \times m_k \vec{v}_k$, with arbitrary velocities $\vec{v}_k$, to conclude that for a system at equilibrium the (macroscopic) velocity of each subsystem must be $\vec{v}_k = \vec{a} + \vec{b} \times \vec{r}_k$ with $\vec{a}$ and $\vec{b}$ vector constants, i.e. a solid-body motion (at rest in a suitable reference state). Mind that the rest state at equilibrium is only at the macroscopic scale (the fluid particle), but there is always an underlying microscopic motion which, in the case of ideal gases, it shows Maxwell-Boltzmann distribution law for molecular speeds).

Proceeding in a similar manner, but now taking control volumes instead of control masses, one may consider the distribution of chemical species and also include the effect of external force fields, to conclude that now $T\partial S / \partial n_i - M_i g z + \tfrac{1}{2} M_i \left(\vec{\Omega} \times \vec{r} \right)^2$ =constant, (with M_i the molar mass of substance i, multiplying the effect of the linear gravity field and the centrifugal force field), what prompts to the definition of the so called chemical potential μ_i (introduced in 1875 by Gibbs):

$$\frac{\mu_i}{T} \equiv \left. \frac{-\partial \mathcal{S}}{\partial n_i} \right|_{U,V} \qquad (2.5)$$

The minus sign in the definition of μ_i is introduced because, contrary to tendency of entropy to increase with increasing energy and volume, entropy should decrease when more particles must share the same energy and volume. As a first approach, one may think of μ_i as a modified concentration c_i of species i in the mixture, but μ_i not only depends on c_i but on the other concentrations c_j in the mixture (and on p and T). The algebraic value of μ_i (sign and absolute value) is of little interest because it depends on these other

mixture parameters, but, in a natural (spontaneous) process, μ_i decreases. For a pure-component system, μ is not an independent variable but a function of p and T.

Entropy measurement

We have introduced above direct links between entropy, that difficult-to-measure statistical variable, S from (1), and some (apparently) easy-to-measure physical variables, by (2.4) and (2.5), what solves the problem of how to measure entropy: by integration of those derivatives. Temperature and pressure measurement details can be found aside. Related to this measurability condition, to be further developed below, is the answer to the possible doubt about the objectivity of entropy as defined by (1): shouldn't it be a subjective measurement, being an information content that is based on probabilities? The answer is that entropy is similar to a probability: it can be assigned a priori by the observer according to his/her knowledge, but it is only valid if it agrees with the accumulative relative frequency from experiments (like for a dice). In brief, we postpone any further statistical interpretation of entropy until Chapter 7: Mixtures, and restrict for the moment entropy measurements to the physical derivatives mentioned.

Joining (2.4) and (2.5) one gets the differential form for the entropy as a function of internal energy, volume and amount of substance (it cannot depend on momentum or mechanical energy since these have arbitrary reference states):

$$\boxed{dS = \frac{1}{T}\,dU + \frac{p}{T}\,dV - \sum_{i=1}^{C} \frac{\mu_i}{T}\,dn_i} \qquad (2.6)$$

This important equation can be understood in the following way. Temperature (or $1/T$) measures the escape tendency of thermal energy (dU), and any temperature gradient forces an energy flux and a corresponding entropy generation (see below) by heat transfer. Pressure (in p/T) measures the escape tendency of mechanical energy (pdV), and any pressure gradient (in the absence of external fields) forces an energy flux and a corresponding entropy generation by friction and viscous dissipation. The chemical potential μ_i of a species i (in μ_i/T) measures the escape tendency of chemical energy ($\mu_i dn_i$), and, any chemical-potential gradient (in the absence of external fields), will force an energy flux and a corresponding entropy generation by mass diffusion.

Substituting the internal energy equation (1.9), in differential form, in (2.6) yields:

$$dS = \frac{dQ + dE_{mdf}}{T} - \sum_{i=1}^{C} \frac{\mu_i}{T}\,dn_i \qquad (2.7)$$

Equation (2.6), or its equivalent (knowing that $S(U)$ is monotonous):

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V + \Sigma\mu_i \mathrm{d}n_i, \qquad (2.8)$$

are sometimes called, indistinctly, the Fundamental Equation of Equilibrium Thermodynamics, although equation (2.2), $S(U,V,n_i)$=maximum for U, V and n_i constant, is more basic since, beyond (2.6) it states that $\mathrm{d}^2S<0$ that has not being enforced yet. In fact, this entropy-maximum principle establishes important bounds

to the values of some thermodynamic variables (e.g. thermal capacities cannot be negative; see System stability in Chap. 4: Thermodynamic potentials). Notice that $S(U,V,n_i)$=maximum, contains all the information on the properties of the system at equilibrium, and that entropy does not depend on total energy but on internal energy, because this is the materials constitutive relation, and it cannot depend on the observer's reference frame. Notice also that for the time being we only care about entropy changes, computed from (2.6) as shown below, but (2.1) defines entropy in absolute terms, relative to the absolute reference, that here is the unique microstate at T=0 K, with the system at its fundamental quantum state (an absolute internal energy reference also).

Exercise 1. Direction of heat transfer

Entropy for perfect substances

Now that entropy has been related to the traditional variables (T,U,p,V) there is no need to compute it from its definition (2.1). For the most important models of incompressible substances and ideal gases, both as perfect calorific substances, (2.6) yields:

$$\text{for an incompressible perfect substance} \quad dS = \frac{1}{T}dU + \frac{p}{T}dV = \frac{mcdT}{T} \Rightarrow \quad S - S_0 = mc\ln\frac{T}{T_0} \tag{2.9}$$

$$\text{for a perfect gas} \quad dS = \frac{1}{T}dU + \frac{p}{T}dV = \frac{mc_v dT}{T} + \frac{mR}{V}dV \Rightarrow \quad S - S_0 = m\left(c_v \ln\frac{T}{T_0} + R\ln\frac{V}{V_0}\right) \tag{2.10}$$

and for a closed system without friction, from equation (2.7):

$$\text{for a reversible process of a closed system} \quad dS = \frac{dQ}{T} \tag{2.11}$$

that was the original definition of entropy by Clausius (he gave it the symbol S, without explanations, even before naming this 'transformation property' entropy).

Entropy generation

For real (i.e. irreversible) processes in a closed system (dn_i=0), (2.7) implies $dS \geq dQ/T$, the so called Clausius inequality, and it is convenient to define an entropy generation or entropy production variable, S_{gen}, by the difference between entropy increase and entropy flow:

$$dS_{gen} \equiv dS - \frac{dQ}{T} \geq 0 \tag{2.12}$$

where the non-negative constraint comes from the fact that for the system plus its environment, isolated as a whole, the total entropy cannot decrease, $dS_{univ}/dt>0$. Sometimes, S_{gen} is labelled S_i, and other times σ; thus, equation (2.12) can be rewritten as $dS=dS_{gen}+dQ/T$ or $dS=dS_i+dS_e$, with $dS_i>0$ being the entropy change due to internal processes (has to be non-negative) and $dS_e=dQ/T$ the entropy change due to external

flow of entropy through the frontier. Notice that the integrated form of (2.12) is $S_{gen}=\Delta S-\int dQ/T$, since only S is a state function (S_{gen} and Q being path integrals). Entropy flow associated to mass flow in open systems is covered in Chap. 5: Control Volume, with the result that (2.12) becomes $dS_{gen}=dS-dQ/T-\Sigma s_e dm_e>0$, with s_e being the specific entropy of the mass entering the system, dm_e, by each of the openings (the summation).

Temperature within the system is assumed uniform in (2.12), as usual in the Thermodynamics of systems at equilibrium; where the system had a non-uniform temperature, a local integration of dQ/T along the frontier should be performed. Another tricky question arises when using uniform temperature systems, and it is where to locate the generation of entropy when heat flows from a system at temperature T to an ambient at temperature T_0; the answer is that an additional interfacial system is needed because the interface has a discontinuity that enclose physical properties (see Exercise 2 for further explanations).

It is very important to understand the meaning of 'reversible', which is a short-hand to 'without entropy generation'. All natural and artificial processes are irreversible, i.e. generate entropy by friction, heat flow or mass flow, and the idealisation of a reversible process in Thermodynamics is similar to the idealisation of a frictionless movement in Mechanics. It does not mean that irreversible processes cannot run backwards; as Newton's apple fallen to ground can be mechanically forced to rise to its tree, so irreversible processes can be thermodynamically forced to recover their initial conditions (even the death of a living being could be reversed from the thermodynamic standpoint; it is just that we presently do not know how, although we know how to make a new glass from the shattered fragments: by melting them).

Entropy generation mechanisms

We have seen that the consequences of thermodynamic equilibrium are the uniformity of temperature, the solid-body motion of the system, and the uniformity of chemical potentials in absence of external fields (what causes the uniformity of pressure in that case). Non-equilibrium implies non-uniformity of those equilibrium parameters, so that entropy generation has to be associated to those non-uniformities, in the most basic or ultimate cause. Table 1 gives a key-summary of the basic mechanisms of entropy generation in the most general case.

Table 1 Consequences of thermodynamic equilibrium, and basic mechanisms of entropy generation.

Consequences of equilibrium	Causes of entropy generation
$\nabla T(\vec{r})=0$	$\nabla T(\vec{r})\neq 0$, i.e. all kinds of heat transfer
$\vec{v}(\vec{r})=\vec{v}_{cm}+\vec{\Omega}_{cm}\times\vec{r}$	$\vec{v}(\vec{r})\neq\vec{v}_{cm}+\vec{\Omega}_{cm}\times\vec{r}$, i.e. any relative motion
$\nabla\left(\mu_i(\vec{r})-M_i\vec{g}\cdot\vec{r}-\tfrac{1}{2}M_i\left(\vec{\Omega}\times\vec{r}\right)^2\right)=0$	$\nabla\left(\mu_i(\vec{r})-M_i\vec{g}\cdot\vec{r}-\tfrac{1}{2}M_i\left(\vec{\Omega}\times\vec{r}\right)^2\right)\neq 0$, i.e. any gradient of this generalised chemical potential, that for a pure substance at rest reduces to $\nabla(p+\rho gz)\neq 0$, and, in absence of external force fields reduces to $\nabla p\neq 0$ (see Gibbs-Duhem equation below).

Exercise 2. Bar between thermal blocks
Exercise 3. Push and release of a piston
Exercise 4. Maximum temperature in a system

GIBBS-DUHEM EQUATION

Equation (2.7), $dU=TdS-pdV+\Sigma\mu_i dn_i$, is also known as Gibbs equation, and it is an homogeneous equation of the first order, i.e. with all the terms proportional to the same power on the size of the system: $U(\lambda S,\lambda V,\lambda n_i)=\lambda U(S,V,n_i)$, which can be integrated to yield:

$$U=TS-pV+\Sigma\mu_i n_i \qquad (2.13)$$

known as Euler equation because of the theorem on integration of homogeneous equation due to Euler. Subtracting Gibbs equation from the total differentiation of the Euler equation yields the so called Gibbs-Duhem equation:

$$0=SdT-Vdp+\Sigma n_i d\mu_i \qquad (2.14)$$

that relates all the intensive variables of the equilibrium state (T,p,μ_i).

In the case of a pure substance and dividing by the amount of substance one gets $0=sdT-vdp+d\mu$ that may explain why temperature and pressure are so familiar concepts and the chemical potential not so much, because for a pure substance μ is not an independent variable.

Fluid-static equation

Substitution of the general conditions for equilibrium ($\nabla T=0$, $\vec{v}=\vec{v}_{cm}+\vec{\Omega}_{cm}\times\vec{r}$ and $\nabla\left(\mu_i - M_i\vec{g}\cdot\vec{r} - \tfrac{1}{2}M_i\left(\vec{\Omega}\times\vec{r}\right)^2\right)=0$ on Gibbs-Duhem equation, yields the generalised fluid-static equation (commonly known as the hydrostatic equation):

$$0=0-Vdp+\Sigma n_i(-M_i g dz+M_i\Omega^2 r dr) \qquad (2.15)$$

For instance, in the case of an incompressible liquid (pure or a mixture), i.e. of constant density $\rho=\Sigma n_i M_i/V$, integration gives:

$$p+\rho gz-\frac{1}{2}\rho\Omega^2 r^2=const \qquad (2.16)$$

Related to that is the natural segregation of a mixture at equilibrium in a force field. At equilibrium in a gravity field $d(\mu_i+M_i gz)=0$, or $\partial\mu_i/\partial p\cdot dp/dz+\partial\mu_i/\partial x_i\cdot dx_i/dz+M_i g=0$, what means, for ideal mixtures ($\partial\mu_i/\partial p=v_i=V/n$, $\partial\mu_i/\partial x_i=RT/x_i$) $d\ln(x_i)/dz=(M_m-M_i)g/(RT)$, where x_i is the molar fraction of species i of molar mass M_i, and M_m is the molar mass of the mixture.

Liquid-vapour equilibrium

For a two-phase equilibrium of a pure substance, e.g. liquid-vapour equilibrium (LVE), the consequences of equilibrium (in absence of external force fields) is the uniformity of T, p and μ, not only in each phase but also across the interfaces, i.e. in VLE $\mu_L(T,p)=\mu_V(T,p)$, establishing a relation between temperature and pressure:

$$p=p_V(T) \qquad (2.17)$$

$p_V(T)$ being the vapour pressure of the pure substance at that temperature. Besides, subtracting Gibbs-Duhem equation in the liquid phase, $0=s_L dT - v_L dp + d\mu$ from that in the vapour phase, $0=s_V dT - v_V dp + d\mu$, it follows that $0=(s_V - s_L)dT - (v_V - v_L)dp$, i.e. the pressure variation with temperature at liquid-vapour equilibrium, is related to the entropy change and volume change in the form:

$$\left.\frac{dp}{dT}\right|_{LVE} = \frac{s_V - s_L}{v_V - v_L} \qquad (2.18)$$

which is named Clapeyron equation, one of the most important thermodynamic relations. Vapour pressure of pure substances is to be analysed in more detail in Chapter 4: Thermodynamic potentials and Chaper 6: Phase change.

System variance

The variance of a thermodynamic system is the minimum number of intensive variables defining its state, i.e. its degrees of freedom.

For a simple compressible substance, i.e. for a constant-composition system, the variance V is two ($V=2$), usually chosen as its temperature and pressure, what means that any other intensive thermodynamic variable can be obtained from them (and the knowledge of the system composition, of course).

For a system with C chemically different components that may coexist in P different phases, the variance V (or degrees of freedom) is given by Gibbs phase rule: $V=2+C-P$. Sometimes F (for freedom) is used instead of V (variance), and Φ instead of P for phases. The explanation is that there appear $2+C$ variables defining the equilibrium state (T, p and μ_i, in Eqs. 2.4-5), and their only dependence is Gibbs-Duhem relation (2.14) for each phase.

If the system can hold R different chemical reactions at equilibrium, Gibbs phase rule extends to $V=2+C-P-R$.

TYPE OF PROBLEMS

Besides housekeeping problems of how to deduce one particular equation from others, and some ancillary exercises from probability and statistics to better grasp the concept of entropy, the types of problems in this chapter are:

1. Find if a particular evolution of a system when some internal or external restrictions are released is possible or not, under the given constraints (e.g. Exercise 1). Finding the speed or duration of the process is also a thermal problem usually addressed by 'extended Thermodynamics' sciences (Heat transfer, Fluid dynamics).
2. Compute entropy changes and entropy generation for a given system between given equilibrium states, and verify that isolated systems (the universe) evolve from lower to greater entropy values (positive entropy generation).
3. Find limit values to particular system variables (imaging zero entropy increase, as in Exercise 3).

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