

On teaching thermodynamics

This content has been downloaded from IOPscience. Please scroll down to see the full text.

2011 Eur. J. Phys. 32 15

(<http://iopscience.iop.org/0143-0807/32/1/002>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 131.156.157.31

This content was downloaded on 25/03/2015 at 04:48

Please note that [terms and conditions apply](#).

On teaching thermodynamics

F Debbasch

ERGA-LERMA UPMC UMP8112, 3 rue Galilée 94200 Ivry, France

E-mail: fabrice.debbasch@gmail.com

Received 1 September 2010, in final form 6 October 2010

Published 8 November 2010

Online at stacks.iop.org/EJP/32/15

Abstract

The logical structure of classical thermodynamics is presented in a modern, geometrical manner. The first and second law receive clear, operatively oriented statements and the Gibbs free energy extremum principle is fully discussed. Applications relevant to chemistry, such as phase transitions, dilute solutions theory and, in particular, the law of mass action, are also addressed in a very detailed and novel manner. The material is best suited to graduate level students and professors, and it brings classical thermodynamics closer to other branches of university physics where geometry plays a key role.

1. Introduction

Classical thermodynamics was developed as a theory of heat engines in the 19th century [1]. Physical sciences and mathematics have since then developed in a dramatic way, but most textbooks fail to take those developments into account and still present thermodynamics in a 19th century oriented manner. The aim of this paper is to present in modern geometrical terms [2, 3] the general basic structure underlying classical thermodynamics; in particular, extensive use is made of differential geometry [4, 5], in both its intrinsic and non-intrinsic aspects.

The presentation is concise and not comprehensive; this is not a course in thermodynamics, but rather an indication of the possible logical construction of a course. The material is aimed at graduate level students and professors and is organized as follows. Pure substances are considered first. The basic geometrical framework and the first and second law are introduced in sections 2 and 3, while first-order transitions are addressed in section 4. The chemical thermodynamics of dilute solutions are discussed in sections 5–7. Section 5 presents the equilibrium theory of solutions while section 6 deals with the Gibbs free energy extremum principle. The latter is used in section 7 to derive the law of mass action. Section 8 is a brief conclusion.

2. General framework: first law

Classical thermodynamics, as developed in the 19th century, focuses on equilibrium states of macroscopic systems. The space of all equilibrium states of a given arbitrary macroscopic

system Σ can be viewed as a real surface or, in more precise mathematical terms, a real differential manifold M_Σ [4, 5]. Equilibrium states of Σ are thus points of M_Σ and, around any point/equilibrium state A , M_Σ ‘looks like’ a domain of \mathbb{R}^d , where the integer d depends on Σ but not on the point A and is called the dimension of M_Σ ; in particular, all points around A can then be charted by using d real coordinates. For example, $d = 3$ for a pure fluid.

The manifold M_Σ does not represent all states of Σ but only equilibrium states. Mathematically speaking, M_Σ is thus embedded in a ‘larger’ space \tilde{M}_Σ whose elements also include non-equilibria. The precise mathematical structure of this larger space depends on the retained model for out-of-equilibrium dynamics and will not be further elaborated upon in this paper. A curve of \tilde{M}_Σ that lies entirely in M_Σ and can thus be interpreted as a succession of equilibrium states is usually called a reversible transformation. Curves that do not lie entirely in M_Σ are called irreversible transformations. All real transformations are irreversible.

Equilibrium physical quantities can be represented by functions defined on M_Σ . All coordinates discussed above and, in particular, the number n of moles are such functions. The first law of thermodynamics essentially states that thermodynamical systems are endowed with an energy E and that E is represented, for equilibrium states, by a real function defined on M_Σ . We will henceforth assume that Σ is at rest in the chosen reference frame, in which case E coincides with the internal energy U of Σ .

3. Pure substances

3.1. Samples with fixed matter content—second law: part 1

Suppose first that the quantity of matter, i.e. that the number of moles, is fixed to an arbitrary value n , and let \tilde{M}_Σ^n and M_Σ^n be the corresponding state spaces. Note that the dimension of M_Σ^n is $d - 1$ if the dimension of M_Σ is d . The restriction of U to M_Σ^n will be denoted by U^n . Consider now two arbitrary points A and B on M_Σ^n and an arbitrary curve C of \tilde{M}_Σ^n that goes from A to B . Non-thermal, i.e. ‘mechanical’, physics associates with any curve C of \tilde{M}_Σ^n joining A and B the work W^n received by the system evolving from A to B on C . Thermodynamics associates a new quantity Q^n to C , defined by $Q^n = U^n(B) - U^n(A) - W^n$. The quantity Q^n is called the heat received by the system Σ in evolving from point A to point B along C . By definition, while both W^n and Q^n generally depend not only on A and B but also on the curve C joining A and B , their sum $W^n + Q^n$ does not depend on C and is simply the difference in internal energy between point B and point A .

Consider now a curve C that joins A and B and lies entirely in M_Σ^n . From non-thermal physics, one knows that the work W^n received by Σ along C can then be written as an integral along the curve C of a differential form w_n , called reversible work at constant n . The difference $q^n = dU^n - w^n$ is called reversible heat at constant n .

The second law deals with the differential form q^n and offers two key inputs. The first of these will be considered now and the second in section 3.2 below.

Second law: part 1. The second law first states that, for all n , there exists a global integrating factor for q^n on M_Σ^n , that this integrating factor does not depend on n , and that it is identical to what we call the inverse thermodynamical temperature T . In other words, for all n , q^n / T is the exact differential of a function S^n defined on M_Σ^n . The set of all S^n s defines a function S on M_Σ , which is called the entropy. Note that Caratheodory’s reasoning [2], popularized notably by M Born, is only local, and therefore fails to ensure the existence of a global thermodynamical entropy [6]. The existence of the entropy thus needs to be postulated.

By definition of the entropy S^n , $q^n = T dS^n$ for all n^1 . Suppose now that non-thermal physics implies $w^n = \sum_{i=1}^l \xi_i d\chi^i$, where the χ s are mechanical variables describing the sample at fixed n^1 . One then obtains $dU^n = T dS^n + \sum_{i=1}^l \xi_i d\chi^i$. It is then natural to use $x^1 = S^n$ and $x^2 = \chi^1 \dots \chi^{l+1} = \chi^l$ on M_Σ^n . Since M_Σ^n is of dimension $d - 1$, this leads to $l = d - 2$. Example: $dU^n = T dS^n - p dV$ for a pure fluid.

3.2. Samples with arbitrary matter content—thermodynamic identity; second law: part 2

We now work again on the full d -dimensional manifold M_Σ of equilibrium states. A coordinate system of M_Σ is $x^1 = S$, $x^2 = \chi^1, \dots, x^{d-1} = \chi^{d-2}$, $x^d = n$. At this stage, the choice of the mechanical coordinates χ is quite arbitrary. Suppose now one can choose all the χ s to be extensive quantities, i.e. quantities that vary linearly with the matter content or number of moles n . In many physical systems, the entropy S is also extensive. Suppose thus that all the x s are extensive. The quantities S, x^2, \dots, n are then called the natural variables of U . The chemical potential μ of the sample is then defined by $\mu = (\partial U / \partial n)_{S, x^2, \dots, x^{d-1}}$ and one thus writes $dU = T dS + \sum_{i=1}^{d-2} \xi_i d\chi^i + \mu dn$. Example: $dU = T dS - p dV + \mu dn$ for a pure fluid. This is the so-called differential form of the thermodynamic identity.

Integral thermodynamic identity. We will henceforth suppose that U is also extensive. Then, for all real $\lambda > 0$, $U(\lambda S, \lambda \chi^1, \dots, \lambda \chi^{d-2}, \lambda n) = \lambda U(S, \chi^1, \dots, \chi^{d-2}, n)$. Differentiating this identity with respect to λ leads to the following integral form of the thermodynamic identity: $U = TS + \sum_{i=1}^{d-2} \xi_i \chi^i + \mu n$. This result is a special case of Euler's lemma on homogeneous functions.

Note that U can replace S as the first extensive coordinate. In other words, both $(S, \chi^1, \dots, \chi^{d-2}, n)$ and $(U, \chi^1, \dots, \chi^{d-2}, n)$ can be used as extensive coordinates on the manifold M_Σ .

Differentiating the integral form of the thermodynamical identity and comparing with the differential form of this identity leads to the Gibbs-Duhem relation $d\mu = -(S/n) dT - \sum_{i=1}^{d-2} (\chi^i/n) d\xi_i$. Example: $d\mu = -(S/n) dT + (V/n) dp$ for a simple pure fluid. This relation suggests that $(T, \xi^1, \dots, \xi^{d-2}, n)$ can be used as coordinates on M_Σ . This can be done as long as the equilibrium describes a single phase of Σ . This point is elaborated upon in sections 3.3 and 4 below.

Second law: part 2. Take two samples Σ_a and Σ_b of the same pure substance and let $x_a = (U_a, \chi_a^1, \dots, \chi_a^{d-2}, n_a)$ and $x_b = (U_b, \chi_b^1, \dots, \chi_b^{d-2}, n_b)$ be their respective *extensive* coordinates. The entropy of a sample of the pure substance is represented by a function $S(x)$. Suppose you can put the two samples together to constitute a single combined system and do so, isolating them from any outside influence. The initial values of the extensive coordinates $x_{a \cup b}$ of the combined system is evidently $x_a + x_b$. The initial value of the entropy $S_{a \cup b}$ of the combined system is $S_a + S_b = S(x_a) + S(x_b)$. It is a fact of experience that, in general, the combined system will evolve from its original state and reach an equilibrium state. Since the combined system is isolated, the values of its extensive coordinates remain constant (remember that, by definition, from mechanics, work is needed to modify the χ s). The second law then states that entropy of the combined system will not generically remain constant and that the equilibrium value of this entropy will be the maximum value compatible with the the constraint $x_{a \cup b} = x_a + x_b$. In particular, $S(x_a + x_b) \geq S(x_a) + S(x_b)$ for all (x_a, x_b) ,

¹ We suppose that the number and nature of these variables do not depend on n and we drop the extra n -index on both the χ 's and the ξ 's, as is customary in mechanics.

the equality being realized in the limit, unrealistic case of reversible transformations of the combined system $\Sigma_{a \cup b}$.

Concavity of the entropy. This last inequality implies that S is a concave function of x . Indeed, choose two arbitrary equilibrium states, of coordinates X_1 and X_2 , and suppose that the d -uples of the form $x_a(\lambda) = \lambda X_1$, $x_b(\lambda) = (1 - \lambda)X_2$, $x_a(\lambda) + x_b(\lambda) = \lambda X_1 + (1 - \lambda)X_2$, $\lambda \in (0; 1)$ are the coordinates of equilibrium states on M_Σ . The second law and the extensivity of the entropy then implies $S(x_a(\lambda) + x_b(\lambda)) = S(\lambda X_1 + (1 - \lambda)X_2) \geq S(\lambda X_1) + S((1 - \lambda)X_2) = \lambda S(X_1) + (1 - \lambda)S(X_2)$, which proves the concavity of S as a function of x . We note that the above inequality is not strict, and that the second law thus does not imply strict concavity of the entropy, but only concavity. Thus, the Hessian of S with respect to x is non-negative, but not necessarily positive definite.

3.3. More on geometry

The only functions on M_Σ introduced so far are U , S , n and the χ s. In particular, the temperature T , the ξ s and the chemical potential μ have only appeared as components of ∇U in the coordinate basis $(\partial/\partial S, \partial/\partial \chi^1, \dots, \partial/\partial \chi^{d-2}, \partial/\partial n)$. Yet, these quantities can also be conceived as functions defined on M_Σ and thus, for instance, used as local coordinates. Take T , for example. The gradient ∇U of U is a field of 1-form. It can thus act on vector fields to deliver scalar fields, i.e. functions defined on M_Σ . By definition, the action of ∇U on the first basis vector $\partial/\partial S$ gives the first component of ∇U in the dual basis, i.e. T . The temperature can thus also be viewed as a function on M_Σ . The same goes for the ξ s (for example, the pressure p) and for the chemical potential μ .

4. First-order phase transitions of pure substances

Let us now show how first-order phase transitions are described in the above framework. For simplicity, we will only consider simple fluids; we choose Σ as a fixed quantity of a simple fluid, say 1 mole. The thermodynamical identity then reads $ds = du/T + (p/T) dv$, where s , u and v are the entropy, internal energy and volume of the mole.

Since the number of moles of Σ is fixed, the dimension of M_Σ is 2; suppose, as was until now implicitly assumed, that (u, v) can be used as local coordinates on M_Σ . We now want to investigate if the couple (T, p) can also be used as local coordinates. The couple (T, p) can be used as coordinates if the change from (u, v) to (T, p) is one-to-one, i.e. if the Jacobian $\partial(T, p)/\partial(u, v)$ is non-vanishing. By the thermodynamical identity, this Jacobian coincides, up to an inessential multiplicative factor, with the determinant of the Hessian of s with respect to (u, v) . Thus, the change from (u, v) to (T, p) is one-to-one, and (T, p) can be used as local coordinates, at all points where the entropy is strictly concave. At other points, T and p are not ‘independent’ quantities, and thus cannot be used together as local coordinates.

We will now see that each domain of M_Σ where the entropy is strictly concave describes one phase of Σ and that, in contrast, domains where the entropy is not strictly concave describe phase equilibria. Indeed, consider a domain $\mathcal{D} \in M_\Sigma$ where the concavity of the entropy is not strict; the transformation $(u, v) \rightarrow (T, p)$ is not one-to-one in \mathcal{D} and, thus, maps the 2D domain \mathcal{D} unto a domain \mathcal{D}' of lesser dimension in the (T, p) plane. There are two possibilities: \mathcal{D}' is either one dimensional, i.e. a curve, or zero dimensional, i.e. a point.

Consider the first case, i.e. \mathcal{D}' is a curve, and let λ be a parameter along this curve. Typical choices include $\lambda = T$ or $\lambda = p$. If one chooses $\lambda = T$, the domain \mathcal{D}' is thus a curve $p_e(T)$, which represents the coexistence of two phases I and II. It is then natural to use λ and

one of the earlier coordinates u or v as coordinates in \mathcal{D} . Say we choose (T, v) . At fixed T , the domain \mathcal{D} then corresponds to an interval $(v_I(T), v_{II}(T))$. The end values $v_I(T)$ and $v_{II}(T)$ are interpreted as the volume per mole in each phase at temperature T and points with $v_I(T) < v < v_{II}(T)$ are interpreted as describing the coexistence of the two phases I and II at temperature T .

Remember now that the system is a pure fluid. To any equilibrium point thus corresponds a value of the chemical potential μ . By the Gibbs–Duhem equality, μ can be viewed as a function of T and p only. Therefore, to all two-phase equilibria occurring at a certain temperature T and its associated pressure $p_e(T)$ corresponds the same value of the chemical potential μ . In particular, if one denotes the chemical potentials of the pure phases I and II by μ_I and μ_{II} , one has $\mu_I(T, p_e(T)) = \mu_{II}(T, p_e(T))$ for all T , from which the Clausius–Clapeyron relation can easily be deduced. Note that the equality of μ_I and μ_{II} is not proved by advocating the theory of thermodynamical potentials (extremum principles) but is rather a simple and direct consequence of the fact that the two-phase equilibria under consideration are equilibria of a single pure substance Σ , that classical thermodynamics postulates that such equilibria are represented mathematically by points on the manifold M_Σ and, therefore, correspond to a single value of the chemical potential μ . Now, of course, representing equilibrium states of pure substances by points on a manifold is consistent with the extremum principles of classical thermodynamics, but it is not a consequence of these principles, at least within the present axiomatic approach to classical thermodynamics.

Suppose now that a two-phase equilibrium domain is not infinite. It can basically terminate in two different ways. The first possibility is that $v_I(T) = v_{II}(T)$ for some temperature T_0 . There is then no difference between both phases beyond T_0 . The single phase that exists beyond T_0 is sometimes called a fluid phase. The other possibility is that the domain \mathcal{D} ends up, for some temperature T_1 , in a domain Δ where (u, v) are mapped into a single point (T_1, p_1) of the (T, p) plane. In practical applications, two more domains describing two-phase equilibria then coalesce into Δ . The domain Δ then describes the coexistence of three phases and the corresponding point (T_1, p_1) is called the triple point.

All standard graphical representations of phase equilibria are thus recovered in a natural way. The geometrical approach makes it, for example, quite clear that two- or three-phase equilibria always correspond to a domain in M_Σ and, thus, to infinities of equilibrium states. It is only when projected unto the (T, p) plane that these infinities become curves (two-phase equilibria) or points (three-phase equilibria). In particular, ‘the’ triple point represents a domain in M_Σ and, thus, an infinity of states where three phases are in equilibrium.

5. Solutions

The thermodynamical theory of dilute solutions is modelled on the theory of ideal gas mixtures. However, it cannot be entirely justified by purely macroscopic arguments and needs an input from statistical physics, as will be seen below.

Let us consider a dilute mixture of k substances in a certain solvent. The index 0 labels quantities pertaining to the solvent and the indices $i \in \{1, \dots, k\}$ label quantities pertaining to the diluted substances. For simplicity, we first consider situations where there are no chemical reactions between the constituents of the mixture, in which case the space M_Σ of equilibrium states of the mixture has dimension $2 + (1 + k) = 3 + k$; we also restrict the discussion to single-phase equilibria and choose $T, p, n_0, n_1, \dots, n_k$ as local coordinates. Extending the arguments below to several phase equilibria is straightforward.

Since the mixture is dilute, $n_i \ll 1$ for all $i = 1, \dots, k$ and we write $U(T, p, n_0, n_1, \dots, n_k) \simeq U(T, p, n_0, 0, \dots, 0) + \sum_{i=1}^k n_i \frac{\partial U}{\partial n_i} \big|_{(T, p, n_0, 0, \dots, 0)}$. By extensivity, $U(T, p, n_0, 0, \dots, 0) = n_0 u_0^0(T, p)$, where $u_0^0(T, p)$ is the proper internal energy of the solvent. Let us define the effective proper internal energies of the solutes by $u_i^*(T, p, n_0) = \frac{\partial U}{\partial n_i} \big|_{(T, p, n_0, 0, \dots, 0)}$ for all $i \in \{1, \dots, k\}$. These *a priori* depend on n_0 . We will henceforth assume that the solute effective proper internal energies do *not* depend on the solvent concentration n_0 and adopt the simpler notation $u_i^*(T, p)$ for all $i = 1, \dots, k$. One can then write $U(T, p, n_0, n_1, \dots, n_k) \simeq n_0 u_0^0(T, p) + \sum_{i=1}^k n_i u_i^*(T, p)$. Let us stress the following. The quantity u_0^0 is the proper internal energy of the solvent considered as a pure substance. In contrast, for $i \geq 1$, u_i^* is not the proper internal energy of constituent i considered as a pure substance but rather an effective proper energy of i at sufficiently high dilutions in the considered solvent. In particular, u_i depends on the solvent for all $i \geq 1$. The difference in superscript traces this important point.

One can similarly expand the volume $V(T, p, n_0, n_1, \dots, n_k)$ ² to get an expression of the form $V(T, p, n_0, n_1, \dots, n_k) \simeq n_0 v_0^0(T, p) + \sum_{i=1}^k n_i v_i^*(T, p)$ and, from this, deduce the expansion of the enthalpy $H(T, p, n_0, n_1, \dots, n_k) \simeq n_0 h_0^0(T, p) + \sum_{i=1}^k n_i h_i^*(T, p)$ with $h_i^*(T, p) = u_i^*(T, p) + p v_i^*(T, p)$ for all $i \in \{0, 1, \dots, k\}$.

The expansion of the entropy cannot be obtained as easily and this is where an input from statistical physics is needed. Let us therefore make an excursion in this direction before proceeding with the classical treatment of mixtures.

A simple statistical treatment of systems at fixed temperature T is offered by the canonical statistics [7, 8]. The key quantity is the partition function, usually denoted³ by $Z(T)$, and is defined by $Z(T) = \sum_{\alpha} \exp(-\beta E_{\alpha})$, where α labels the eigenstates of the Hamiltonian for the system under consideration and $\beta = (k_B T)^{-1}$ is the inverse temperature.

The basic assumption underlying the theory of dilute mixtures is that, in any eigenstate of the Hamiltonian of the mixture, each solvent or solute particle can be assigned a separate, effective one-particle energy, and that the one-particle energies accessible to both solvent and solute particles do not depend on the various concentrations. Naturally, these one-particle energies are *not* identical to the energies the particles may have as free entities. Thus, the particles are allowed to see each other but retain some sort of individuality. The possible energies for solvent particles depend only on the solvent, but the possible energies of the solutes depend on both the solute and the solvent.

This simplifying hypothesis entails that the total partition function $Z(T)$ of the system decomposes into a product of separate partition functions $z_i(T)$ for each constituent of the mixture, and each $z_i(T)$ takes the form $z_i(T) = \zeta_i(T)/N_i!$, where N_i is the number of i -‘particles’ (atoms, molecules, ions) in the mixture and $\zeta_i(T)$ is the so-called reduced partition function associated with a single i -‘particle’⁴.

The internal energy U , free energy F and entropy S of the mixture can be computed from $Z(T)$ by the standard relations $U = -\partial(\ln Z)/\partial\beta$, $F = -(\ln Z)/\beta$ and $S = (U - F)/T$. A direct calculation then shows that $S(T, p, n_0, n_1, \dots, n_k) = n_0 s_0^0(T, p) + \sum_{i=1}^k n_i s_i^*(T, p) - R \sum_{i=0}^k n_i \ln(n_i/n)$, where $n = \sum_{i=0}^k n_i$ is the total mole number and $R = \mathcal{N} k_B$ is the ideal gas constant (\mathcal{N} is the Avogadro number); for all $i \in \{1, \dots, k\}$, the effective proper entropy s_i^* is linked to the effective proper internal energy u_i^* and the effective proper volume v_i^* by $ds_i^* = du_i^*/T + (p/T) dv_i^*$ and, similarly, $ds_0^0 = du_0^0/T + (p/T) dv_0^0$.

² Remember $(T, p, n_0, n_1, \dots, n_k)$ are coordinates on M_{Σ} .

³ From the German *Zustandsumme*, which translates as ‘state sum’.

⁴ We have implicitly assumed that the number of energy eigenstates open to an i -particle is much greater than the number N_i of i -particles. This condition is realized in all standard practical chemical applications.

The straightforward extension of the thermodynamic identity to mixtures reads $U = TS - pV + \sum_{i=0}^k \mu_i n_i$; introducing for all $i \in \{0, 1, \dots, k\}$ the concentration $c_i = n_i/n$ and combining the thermodynamic identity with the above expressions for U , V and S leads to

$$\mu_i(T, p, c_0, c_1, \dots, c_k) = \mu_i^*(T, p) + RT \ln c_i \quad (1)$$

for all $i \in \{1, \dots, k\}$ and

$$\mu_0(T, p, c_0, c_1, \dots, c_k) = \mu_0^0(T, p) + RT \ln c_0 \simeq \mu_0^0(T, p) - RT \sum_{i=1}^k c_i, \quad (2)$$

with $\mu_0^0(T, p) = u_0^0(T, p) - Ts_0^0(T, p) + pv_0^0(T, p)$ and $\mu_i^*(T, p) = u_i^*(T, p) - Ts_i^*(T, p) + pv_i^*(T, p)$. Note that all $k + 1$ chemical potentials depend only on the intensive variables characterizing the state of the mixture.

6. Gibbs free energy as thermodynamic potential

The theory of thermodynamical potentials is very general and aims to characterize constrained equilibrium states of thermodynamical systems as extrema of various functions defined on the manifold of equilibria. We will not develop the general theory in this paper but rather focus on systems evolving at fixed external temperature and pressure, and thus address most direct chemical applications of classical thermodynamics.

A source of heat or heat bath is a system (i) whose transformations are all reversible and (ii) that can deliver heat without modifying its temperature. Similarly, a source of pressure work is a system (i) whose transformations are all reversible and (ii) that can deliver pressure work without modifying its pressure. In practice, only systems that are much larger than those with which they interact can be treated as sources. A typical example is the atmosphere, which can be modelled as a work and heat source for its interactions with all of the usual thermodynamical systems studied in laboratories.

Consider thus a thermodynamical system Σ in contact with a heat and work source A (conveniently called atmosphere) of temperature T_A and pressure p_A , and suppose that the influence of other systems on Σ and on A can be neglected. The combined system $C = \Sigma \cup A$ is then isolated. Its internal energy is constant and its entropy can only increase. Assuming the extensivity of U and S for both systems, this transcribes into $\Delta U_C = \Delta U_\Sigma + \Delta U_A = 0$ and $\Delta S_C = \Delta S_\Sigma + \Delta S_A \geq 0$. Note that one also has $\Delta V_C = \Delta V_\Sigma + \Delta V_A = 0$.

Let us focus first on situations where Σ is initially in an equilibrium state, i.e. a point of M_Σ , but where C is not. The combined system will thus evolve towards an equilibrium point of M_C and we want to characterize this point. Since the atmosphere undergoes a reversible transformation, $\Delta U_A = T_A \Delta S_A - p_A \Delta V_A$. Combining this with the energy and volume conservation for the combined system C leads to $-\Delta U_\Sigma = T_A \Delta S_A + p_A \Delta V_\Sigma$. Extracting ΔS_A from this equality and inserting it into $\Delta S_C = \Delta S_\Sigma + \Delta S_A \geq 0$ leads to

$$\Delta S_\Sigma - \frac{1}{T_A} (\Delta U_\Sigma + p_A \Delta V_\Sigma) \geq 0. \quad (3)$$

Let us introduce the function G^A , defined on M_Σ by $G^A = U - T_A S + p_A V$. Here, the quantities U , S and V are the internal energy, entropy and volume of Σ , respectively, while T_A and p_A are the temperature and pressure of A and are thus constant functions on M_Σ . The function G^A is called the generalized Gibbs free energy of Σ in contact with the atmosphere A ; the letter A is used as an upper (as opposed to lower) index to trace the fact that the function G^A depends on the characteristics of the atmosphere A , but pertains to the system Σ , and not

to A . Introducing the temperature T and the pressure p of Σ , one can also construct the Gibbs free energy G of Σ , defined by $G = U - TS + pV$. The functions G^A and G coincide only at points of M_Σ where $T = T_A$ and $p = p_A$.

The above inequality (3) transcribes into $\Delta G^A \leq 0$, i.e. that the equilibrium state reached by the combined system C corresponds, on M_Σ , to a minimum of the function G^A .

Suppose now that the initial state of Σ is not an equilibrium point of M_Σ but that an internal energy, an entropy and a volume can nevertheless be assigned to it. This is, for example, the case when the initial state of Σ has been obtained by extracting Σ from a larger system that was itself in equilibrium. If that is the case, the above reasoning still applies and the final point reached by C can still be characterized as a minimum of G^A . If the initial (out-of-equilibrium) state of Σ can also be assigned a temperature and a pressure, and if these are equal to the temperature and the pressure of the source, then the inequality $\Delta G^A \leq 0$ becomes equivalent to $\Delta G \leq 0$ (for the system Σ). This last form of the minimum principle will be used in the next section when dealing with chemical reactions. Note that the function G used in this form of the minimum principle is defined both at equilibrium (final point) and out-of-equilibrium (initial point) and is thus, physically and mathematically speaking, an extension of the standard Gibbs free energy. It is nevertheless customary to use the same letter G for the standard equilibrium Gibbs free energy and its out-of-equilibrium extension.

7. Chemical reactions

Consider a dilute mixture of k solutes in a given solvent and suppose a chemical reaction of the form $\alpha_1 R_1 + \dots + \alpha_m R_m \rightarrow \alpha_{m+1} R_{m+1} + \dots + \alpha_k R_k$ takes place in the mixture. This reaction can be formally represented by $\sum_{i=1}^k \nu_i R_i = 0$ with $\nu_i = -\alpha_i$ for $1 \leq i \leq m$ and $\nu_i = \alpha_i$ for $m+1 \leq i \leq k$.

If there were no chemical reaction, the dimension of the equilibrium manifold would be $3 + k$ (see above, section 5). Consider on this manifold a coordinate system of the form $(T, p, \lambda, n_0, \dots, n_{j-1}, n_{j+1}, \dots, n_k) = (T, p, \lambda, X)$, where λ is the degree of conversion of the reaction and X is a k -uple. Note that λ is an intensive coordinate. We know by experience that, for given values of the other coordinates, there is a single equilibrium state, corresponding to a certain value $\lambda_e(T, p, X)$ of λ . This means that the equilibrium manifold of the mixture where the reaction takes place is not of dimension $3 + k$ but of dimension $2 + k$. If there were r reactions, the equilibrium manifold of the mixture would be $3 + k - r$ dimensional.

Suppose again $r = 1$. The law of mass action gives the equation for this $2 + k$ manifold viewed as a sub-manifold of the original, larger $3 + k$ manifold, in terms of the original coordinates (T, p, n_0, \dots, n_k) . (The equation of this sub-manifold in terms of the variables (T, p, λ, X) is simply $\lambda = \lambda_e(T, p, X)$.)

Let us now explicitly derive the law of mass action. The functions $c_i = n_i/n$ translate into functions $c_i(T, p, \lambda, X)$. Their equilibrium values $c_{ie}(T, p, X) = c_i(T, p, \lambda_e(T, p, X), X)$ are physical. On the contrary, the out-of-equilibrium values of the functions $c_i(T, p, \lambda, X)$ are not necessarily physical, if only because out-of-equilibrium states are not necessarily homogeneous.

All relations derived in section 5 make sense at equilibrium, i.e. for $\lambda = \lambda_e(T, p, X)$. Suppose now that they also make sense for values of λ close to, but different from, λ_e , say $\lambda = \lambda_e(T, p, X) + d\lambda$. Suppose in particular that the chemical potentials are defined for these homogeneous, close to equilibrium but out-of-equilibrium states, and that relations (1) and (2) remain valid with the equilibrium concentrations $c_{ie}(T, p, X)$ replaced by $c_i(T, p, \lambda_e(T, p, X) + d\lambda)$. A total Gibbs free energy $G = \sum_{i=1}^k n_i \mu_i$ can then also be assigned to these states and can be viewed as a function of T, p, λ and X . Let us stress again

that this function G is *not* the standard, equilibrium free Gibbs energy but an extension of it, defined for both equilibrium and out-of-equilibrium states.

Consider now a relaxation from one of these out-of-equilibrium states towards the equilibrium. We know from section 6 that the out-of-equilibrium extension of the Gibbs free energy is then the correct thermodynamical potential. This implies that the equilibrium corresponds to a minimum of the extended Gibbs free energy G with respect to λ at fixed T , p and X . If the degree of conversion of the reaction varies by $d\lambda$, the numbers of moles vary by $dn_i = v_i d\lambda$. Extremizing \tilde{G} with respect to λ thus leads to $\sum_{i=1}^k v_i \mu_i = 0$. Using equation (2) to make explicit the dependence of the chemical potentials on the concentrations, one obtains the law of mass action $\prod_{i=1}^k c_{ie}^{v_i} = K(T, p)$ with $\ln K(T, p) = -1/(RT) \sum_i v_i \mu_i^*(T, p)$ (if the solvent is one of the reactants, the corresponding μ^* has of course to be replaced by μ_0). The volume, enthalpy and Gibbs free energy variations of the reaction are defined by $\Delta_r V = \sum_i v_i v_i^*$, $\Delta_r H = \sum_i v_i h_i^*$, $\Delta_r G = \sum_i v_i \mu_i^*$. The first two quantities fix the pressure and temperature dependence of $\ln K$. Indeed, by a straightforward extension of Gibbs–Duhem inequality, $(\partial \mu_i^*/\partial p)_T = v_i^*$ and $(\partial \mu_i^*/\partial T)_p = -s_i^*$ so that $(\partial \ln K/\partial p)_T = -\Delta_r V/(RT)$ and $(\partial \ln K/\partial T)_p = +\Delta_r H/(RT^2)$. If the solution can be regarded as incompressible, $\Delta_r V \simeq 0$ and K depends only on the temperature T .

8. Conclusion

We have presented the logical structure of classical thermodynamics in a modern, geometrical manner. We have given clear, operatively oriented statements of the first and second laws and offered a fully detailed derivation of the Gibbs free energy extremum principle. We have also addressed several basic applications relevant to chemistry. In particular, first-order phase transitions, dilute solutions theory and the law of mass action have been the subject of full and novel discussions.

As mentioned in the introduction, this paper does not constitute a course in thermodynamics but, at best, guidelines for such a course. Various extensions are necessary before such a task can be undertaken. First, the link between statistical physics and the modern, geometrical approach to classical thermodynamics should be explored in detail, both for equilibrium and out-of-equilibrium states, leading to new presentations of dynamical theories of continuous media, both non-relativistic and relativistic [9]. The connections of the modern, geometrical approach with the body of work conventionally known as ‘rational thermodynamics’ [6, 10, 11] should also be explored in full.

Acknowledgments

It is a pleasure to acknowledge the help of C Chevalier in preparing this manuscript. This work has been funded by the ANR grant ProbaGeo.

References

- [1] Truesdell C and Bharata S 1977 *The Concepts and Logic of Classical Thermodynamics as a Theory of Heat Engines* (Berlin: Springer)
- [2] Straumann N 1986 *Thermodynamik* (Berlin: Springer)
- [3] Scheck F 2008 *Theoretische Physik 5: Statistische Theorie der Wärme* (Berlin: Springer)
- [4] Dubrovin B A, Novikov S P and Fomenko A T 1984 *Modern Geometry—Methods and Applications* (Berlin: Springer)
- [5] Schutz B 1980 *Geometrical Methods of Mathematical Physics* (Cambridge: Cambridge University Press)

- [6] Truesdell C 1984 *Rational Thermodynamics* (Berlin: Springer)
- [7] Landau L D and Lifshitz E M 1980 *Statistical Physics* 3rd edn (Amsterdam: Elsevier)
- [8] Huang K 1987 *Statistical Mechanics* 2nd edn (New York: Wiley)
- [9] Debbasch F 2009 *News and Views Nat. Phys.* **5** 708–9
- [10] Serrin J 1986 *New Perspectives in Thermodynamics* (Berlin: Springer)
- [11] Silhavy M 2002 *The Mechanics and Thermodynamics of Continuous Media* (Berlin: Springer)