

Thermodynamics

– Understanding –

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Objective: To understand the first and second principles. Starting point: Explanation of what a differential form is, exact (like dU or dS), or non-exact (like δQ and δW).

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The notation $g := f$ means “ g is defined by $g = f$ ”.

1 The space of linear forms

The finite dimensional vector space E , $\dim E = n \in \mathbb{N}^*$, will be either the usual geometric space \mathbb{R}^3 or the space \mathbb{R}^n of thermodynamic variables $T, P, V, n, N, \mu, \dots$ (\vec{e}_i) $_{i=1,\dots,n}$ $\stackrel{\text{noted}}{=} (\vec{e}_i)$ will be a Cartesian basis in E , and a vector $\vec{v} = \sum_{i=1}^n v_i \vec{e}_i \in E$ will be represented by its matrix column $[\vec{v}] = \begin{pmatrix} v_1 \\ \vdots \\ v_n \end{pmatrix}$.

1.1 The dual space $E^* = \mathcal{L}(E; \mathbb{R})$ of linear forms

Recall: If \mathcal{X} and \mathcal{Y} are two sets then $(\mathcal{F}(\mathcal{X}; \mathcal{Y}), +, \cdot) \stackrel{\text{noted}}{=} \mathcal{F}(\mathcal{X}; \mathcal{Y})$ is the vector space of functions from \mathcal{X} to \mathcal{Y} where the sum $f + g$ of the functions f and g is defined by $(f + g)(x) := f(x) + g(x)$, and the exterior multiplication $\lambda \cdot f \stackrel{\text{noted}}{=} \lambda f$ of a scalar λ and a function f is defined by $(\lambda \cdot f)(x) := \lambda(f(x))$.

Definition 1.1 A linear form ℓ on E is a linear real valued function $\ell : E \rightarrow \mathbb{R}$, i.e. a function $\ell \in \mathcal{F}(E; \mathbb{R})$ such that $\ell(\vec{v} + \lambda \vec{w}) = \ell(\vec{v}) + \lambda \ell(\vec{w})$ for all $\vec{v}, \vec{w} \in E$ and $\lambda \in \mathbb{R}$.

The space of linear forms on E is called $\mathcal{L}(E; \mathbb{R}) \stackrel{\text{noted}}{=} E^*$, and

$$\ell(\vec{v}) \stackrel{\text{noted}}{=} \ell \cdot \vec{v}, \quad (1.1)$$

the (external) dot notation $\ell \cdot \vec{v}$ being used because of the “distributivity type property characterizing linearity”: $\ell(\vec{v} + \lambda \vec{w}) = \ell \cdot \vec{v} + \lambda \ell \cdot \vec{w}$.

E^* is a vector space, sub-space of $\mathcal{F}(E^*; \mathbb{R})$, easy proof.

Interpretation: A linear form $\ell \in E^*$ is a measuring tool: It measures vectors $\vec{v} \in E$ (value $\ell \cdot \vec{v} \in \mathbb{R}$).

Dimension calculus: • The “dimension” (length, temperature, pressure, volume...) of a vector $\vec{v} \in E$ is denoted $\{\vec{v}\}$. So a vector \vec{v}_2 which has the same dimension satisfies $\{\vec{v}_2\} = \{\vec{v}\}$.

• If $\lambda \in \mathbb{R}$, then $\{\lambda\} \stackrel{\text{noted}}{=} 1$ (no dimension, or dimension of the arrival space \mathbb{R} , e.g. energy). “Dimension calculus”: If $\vec{v}_2 = \lambda \vec{v}$, where $\lambda \in \mathbb{R}$, then $\{\vec{v}_2\} = \{\lambda \vec{v}\} = \{\lambda\} \{\vec{v}\} = 1 \{\vec{v}\} = \{\vec{v}\}$ as expected (\vec{v}_2 and \vec{v} have the same dimension).

• If $\ell \in E^*$ and $\vec{v} \in E$ then $\ell \cdot \vec{v} \in \mathbb{R}$, so $1 = \{\ell \cdot \vec{v}\} = 1$, and “dimension calculus”: $\{\ell \cdot \vec{v}\} = \{\ell\} \{\vec{v}\}$ where $\{\ell\}$ is the dimension of ℓ , so

$$\{\ell\} = \{\vec{v}\}^{-1}. \quad (1.2)$$

So, the dimension of a linear form is the inverse of the dimension of a vector. In other words, the dimension of a “covariant” vector (= a vector in E^* i.e. a linear form) is the inverse of the dimension of a “contravariant” vector (= a vector in E).

• The dimension of a bilinear form $g : (\vec{u}, \vec{v}) \in E \times E \rightarrow g(\vec{u}, \vec{v}) = (\vec{u}, \vec{v})_g \in \mathbb{R}$ is given by $\{g(\vec{u}, \vec{v})\} = 1$ (dimension of a real); And $\{g(\vec{u}, \vec{v})\} = \{g\} \{\vec{u}\} \{\vec{v}\}$ (dimension calculus), thus

$$\{g\} = \frac{1}{\{\vec{v}\}^2} = \{\ell\}^2. \quad (1.3)$$

1.2 Dual basis

(\vec{e}_i) in E being a basis in E , let $\pi_i \in E^*$ be the projection on $\text{Vect}\{\vec{e}_i\}$ parallel to the other directions, i.e. $\pi_i \in E^*$ (linear form) is defined by,

$$\pi_i \cdot \vec{e}_j = \delta_{ij}, \quad (1.4)$$

for all $i, j = 1, \dots, n$, i.e. $\pi_i(\vec{e}_i) = 1$, and $\pi_i(\vec{e}_j) = 0$ if $i \neq j$. Hence, with $\vec{v} = \sum_{j=1}^n v_j \vec{e}_j$ and π_i being linear, $\pi_i(\vec{v}) = \pi_i(\sum_{j=1}^n v_j \vec{e}_j) = \sum_{j=1}^n v_j \pi_i(\vec{e}_j) = \sum_{j=1}^n v_j \delta_{ij}$, thus

$$\pi_i \cdot \vec{v} = v_i. \quad (1.5)$$

So π_i is the (linear) tool that gives the i -th component of a vector relative to (\vec{e}_i) .

Example 1.2 $\vec{X} = T\vec{e}_1 + P\vec{e}_2 \in \mathbb{R}^2$, where \vec{e}_1 models 1 Kelvin degree and \vec{e}_2 models 1 Pascal, gives: $\pi_1(\vec{X}) = T$ the temperature in Kelvin and $\pi_2(\vec{X}) = P$ the pressure in Pascal. ■

Proposition 1.3 (and definition) $(\pi_i)_{i=1, \dots, n}$ is a basis E^* , called the dual basis of the basis (\vec{e}_i) . And if $\ell \in E^*$ then

$$\ell = \sum_i \ell_i \pi_i, \quad \text{written} \quad [\ell] = (\ell_1 \quad \dots \quad \ell_n), \quad \text{with} \quad \ell_j = \ell \cdot \vec{e}_j. \quad (1.6)$$

the row matrix $[\ell]$ being the matrix of ℓ (relative to the basis (π_i)). Thus, for all $\vec{v} = \sum_i v_i \vec{e}_i$,

$$\ell \cdot \vec{v} = \sum_i \ell_i v_i = [\ell] \cdot [\vec{v}] \quad (\text{matrix calculation rule}), \quad (1.7)$$

the last equality with the usual product rule: (matrix $1 * n$) \times (matrix $n * 1$) = (matrix $1 * 1$).

Proof. 1- The π_i are linearly independent: If $a_1, \dots, a_n \in \mathbb{R}$ and $\sum_{i=1}^n a_i \pi_i = 0$ then $\sum_{i=1}^n a_i \pi_i(\vec{e}_j) = 0$, thus $\sum_{i=1}^n a_i \delta_{ij} = 0$, thus $a_j = 0$, for all j .

2- The π_i span E^* : Let $\ell \in \mathbb{R}^{n*}$, let $\ell_i := \ell(\vec{e}_i)$, let $g := \sum_{i=1}^n \ell_i \pi_i$; Thus g is linear (trivial) and $g(\vec{e}_j) = \sum_{i=1}^n \ell_i \pi_i(\vec{e}_j) = \sum_{i=1}^n \ell_i \delta_{ij} = \ell_j$ thus $g(\vec{e}_j) = \ell(\vec{e}_j)$, for all j , thus $g = \ell$, thus $\ell = \sum_{i=1}^n \ell_i \pi_i$.

Thus $(\pi_i)_{i=1, \dots, n}$ is a basis in E^* , and $\ell = \sum_{i=1}^n \ell_i \pi_i$ gives $\ell(\vec{e}_j) = \ell_j$

And $\ell \cdot \vec{v} = (\sum_j \ell_j \pi_j) \cdot (\sum_i v_i \vec{e}_i) = \sum_{ij} \ell_j v_i \pi_j(\vec{e}_i) = \sum_{ij} \ell_j v_i \delta_{ij} = \sum_j \ell_j v_j = [\ell] \cdot [\vec{v}]$. ■

1.3 Cartesian setting: Notations for the dual basis

- In the geometric space if the variables names are x, y, \dots then

$$\pi_1 \stackrel{\text{noted}}{=} dx, \quad \pi_2 \stackrel{\text{noted}}{=} dy, \dots \quad (1.8)$$

- In the thermodynamic space if the variables names are T, P, \dots then

$$\pi_1 \stackrel{\text{noted}}{=} dT, \quad \pi_2 \stackrel{\text{noted}}{=} dP, \dots \quad (1.9)$$

2 Differential

2.1 Definition and partial derivatives

Definition 2.1 Let Ω be an open set in E . $\phi \in \mathcal{F}(\Omega, \mathbb{R})$ is differentiable at $\vec{x}_0 \in E$ iff there exists a linear form $\ell_{\vec{x}_0} \stackrel{\text{noted}}{=} d\phi(\vec{x}_0) \in E^* = \mathcal{L}(E; \mathbb{R})$, called the differential of ϕ at \vec{x}_0 , s.t., for all \vec{x} near \vec{x}_0 ,

$$\phi(\vec{x}) = \phi(\vec{x}_0) + d\phi(\vec{x}_0) \cdot (\vec{x} - \vec{x}_0) + o(\|\vec{x} - \vec{x}_0\|). \quad (2.1)$$

Then (2.1) is called the first order Taylor development of ϕ near \vec{x}_0 , and the affine function $a_{\vec{x}_0} : \mathbb{R}^n \rightarrow \mathbb{R}$ defined by $a_{\vec{x}_0}(\vec{x}) = \phi(\vec{x}_0) + d\phi(\vec{x}_0) \cdot (\vec{x} - \vec{x}_0)$ is called the affine approximation of ϕ near \vec{x}_0 (the graph of $a_{\vec{x}_0}$ is the tangent plane of ϕ at \vec{x}_0). In other words, a function ϕ is differentiable at \vec{x}_0 iff its graph admits a tangent plane at \vec{x}_0 .

Definition 2.2 If ϕ is differentiable at all points in Ω , then ϕ is differentiable in Ω . The differential of ϕ is then the function $d\phi : \left\{ \begin{array}{l} \Omega \rightarrow \mathbb{R}^{n*} \\ \vec{x} \rightarrow d\phi(\vec{x}) := \ell_{\vec{x}} \end{array} \right\}$. Moreover if $d\phi$ is continuous at any $\vec{x} \in \Omega$ then ϕ is said to be C^1 in Ω , i.e. $\phi \in C^1(\Omega; \mathbb{R})$ the space of C^1 functions in Ω .

(2.1) gives, for all $\vec{v} \in \mathbb{R}^n$,

$$\phi(\vec{x}_0 + h\vec{v}) = \phi(\vec{x}_0) + h d\phi(\vec{x}_0) \cdot \vec{v} + o(h), \quad (2.2)$$

thus

$$d\phi(\vec{x}_0) \cdot \vec{v} = \lim_{h \rightarrow 0} \frac{\phi(\vec{x}_0 + h\vec{v}) - \phi(\vec{x}_0)}{h} \stackrel{\text{noted}}{=} \partial_{\vec{v}} \phi(\vec{x}_0) \stackrel{\text{noted}}{=} \frac{\partial \phi}{\partial \vec{v}}(\vec{x}_0). \quad (2.3)$$

Definition 2.3 $d\phi(\vec{x}) \cdot \vec{v}$ is the directional derivative of ϕ in the direction \vec{v} at \vec{x} . And the i -th partial derivative of ϕ at \vec{x} is

$$d\phi(\vec{x}) \cdot \vec{e}_i \stackrel{\text{noted}}{=} \partial_i \phi(\vec{x}) \stackrel{\text{noted}}{=} \frac{\partial \phi}{\partial \vec{e}_i}(\vec{x}) \stackrel{\text{noted}}{=} \frac{\partial \phi}{\partial x_i}(\vec{x}). \quad (2.4)$$

This defines $\partial_i \phi \stackrel{\text{noted}}{=} \frac{\partial \phi}{\partial x_i} : \left\{ \begin{array}{l} \Omega \rightarrow \mathbb{R} \\ \vec{x} \rightarrow d\phi(\vec{x}) \cdot \vec{e}_i \end{array} \right\}$ called the i -th partial derivative of ϕ .

2.2 Components of a differential in the dual basis

(\vec{e}_i) is a Cartesian basis in \mathbb{R}^n , (π_i) is its dual basis (in \mathbb{R}^{n*}), ϕ is differentiable at $\vec{x} \in \Omega$. With (1.6):

Corollary 2.4 The components of $d\phi(\vec{x}) \in \mathbb{R}^{n*}$, with respect to the dual basis (π_i) , are the $\frac{\partial \phi}{\partial x_i}(\vec{x})$:

$$d\phi(\vec{x}) = \frac{\partial \phi}{\partial x_1}(\vec{x}) \pi_1 + \dots + \frac{\partial \phi}{\partial x_n}(\vec{x}) \pi_n, \quad (2.5)$$

i.e. $[d\phi(\vec{x})] = \left(\frac{\partial \phi}{\partial x_1}(\vec{x}) \quad \dots \quad \frac{\partial \phi}{\partial x_n}(\vec{x}) \right)$, row matrix called the *Jacobian matrix* of ϕ at \vec{x} . With $\pi_i \stackrel{\text{noted}}{=} dx_i$ (2.5) reads:

$$d\phi(\vec{x}) = \frac{\partial \phi}{\partial x_1}(\vec{x}) dx_1 + \dots + \frac{\partial \phi}{\partial x_n}(\vec{x}) dx_n. \quad (2.6)$$

And $d\phi(\vec{x}) \cdot \vec{v} = \frac{\partial \phi}{\partial x_1}(\vec{x}) v_1 + \dots + \frac{\partial \phi}{\partial x_n}(\vec{x}) v_n = [d\phi(\vec{x})] \cdot [\vec{v}]$ (matrix product) when $\vec{v} = \sum_{i=1}^n v_i \vec{e}_i$.

Example 2.5 Suppose that the pressure P depends on the temperature T and volume V : So $P = \tilde{P}(T, V)$ where $\tilde{P} : \left\{ \begin{array}{l} \mathbb{R}^2 \rightarrow \mathbb{R} \\ \vec{X} = (T, V) \rightarrow P = \tilde{P}(\vec{X}) = \tilde{P}(T, V) \end{array} \right\}$. With $(\pi_1, \pi_2) \stackrel{\text{noted}}{=} (dT, dV)$ (dual basis), $d\tilde{P}(\vec{X}) \stackrel{(2.6)}{=} \frac{\partial \tilde{P}}{\partial T}(\vec{X}) dT + \frac{\partial \tilde{P}}{\partial V}(\vec{X}) dV$ (as soon as \tilde{P} is differentiable at \vec{X}), i.e.

$$d\tilde{P}(T, V) = \frac{\partial \tilde{P}}{\partial T}(T, V) dT + \frac{\partial \tilde{P}}{\partial V}(T, V) dV, \quad \text{i.e.} \quad [dP(T, V)] = \left(\frac{\partial P}{\partial T}(T, V) \quad \frac{\partial P}{\partial V}(T, V) \right). \quad (2.7)$$

Thermodynamical notations:

$$dP = \frac{\partial P}{\partial T}|_V dT + \frac{\partial P}{\partial V}|_T dV, \quad \text{i.e.} \quad [dP] = \left(\frac{\partial P}{\partial T}|_V \quad \frac{\partial P}{\partial V}|_T \right), \quad (2.8)$$

which implicitly tells that P depends on the (independent) variables T and V . ▀

3 Differential forms

3.1 Definition

Definition 3.1 Ω being an open set in E , A differential form in Ω is function $\alpha \in \mathcal{F}(E; E^*)$. So

$\alpha(\vec{x}) : \left\{ \begin{array}{l} E \rightarrow \mathbb{R} \\ \vec{v} \rightarrow \alpha(\vec{x})(\vec{v}) \stackrel{\text{noted}}{=} \alpha(\vec{x}) \cdot \vec{v} \end{array} \right\}$ for all $\vec{x} \in \Omega$, dot notation since $\alpha(\vec{x})$ is a linear form, cf. (1.1).

Particular case: If $\exists \phi \in C^1(\Omega; \mathbb{R})$ s.t. $\alpha = d\phi$ (i.e. if α derives from a potential ϕ), then α is said to be exact. Otherwise α is not exact.

Components. $(\pi_i) \stackrel{\text{noted}}{=} (dx_i)$ being the dual basis of a Cartesian basis (\vec{e}_i) in E , cf. (1.4), (1.1) gives:

$$\alpha(\vec{x}) = \alpha_1(\vec{x}) dx_1 + \dots + \alpha_n(\vec{x}) dx_n, \quad \text{where} \quad \alpha_i(\vec{x}) := \alpha(\vec{x}) \cdot \vec{e}_i \quad (\text{the components}), \quad (3.1)$$

i.e. $[\alpha(\vec{x})] = \left(\alpha_1(\vec{x}) \quad \dots \quad \alpha_n(\vec{x}) \right)$ (row matrix).

Example 3.2 (Non exact differential form.) $n = 2$; Consider the differential form (“dissipative energy”)

$$\alpha(x, y) = -y dx + x dy, \quad \text{i.e.} \quad \alpha(x, y) \cdot \vec{e}_1 = -y \quad \text{and} \quad \alpha(x, y) \cdot \vec{e}_2 = x. \quad (3.2)$$

This differential form is **not** exact; If it were: $\exists \phi \in C^1$ s.t. $\alpha = d\phi$, so $\frac{\partial \phi}{\partial x}(\vec{x}) = -y$ and $\frac{\partial \phi}{\partial y}(\vec{x}) = x$. And $\frac{\partial \phi}{\partial x}(\vec{x}) = -y$ gives $\phi(\vec{x}) = -yx + g(y)$ for some C^1 function g since $\phi \in C^1$. Hence $\frac{\partial \phi}{\partial y}(\vec{x}) = -x + g'(y)$; Thus $\frac{\partial \phi}{\partial y}(\vec{x}) = x$ gives $-x + g'(y) = x$, thus $g'(y) = 2x$ for all $\vec{x} = (x, y) \in \Omega$ (not empty): Absurd (take $\vec{x}_1 = (x_1, y)$ and $\vec{x}_2 = (x_2, y)$ with $x_1 \neq x_2$ which gives $g'(y) \neq g'(y) \dots$). Thus α is not exact. (Remark: If you looked for a $\phi \in C^2$ then Schwartz’s Theorem gives $\frac{\partial \frac{\partial \phi}{\partial x}}{\partial y}(\vec{x}) = \frac{\partial \frac{\partial \phi}{\partial y}}{\partial x}(\vec{x})$, then $-1 = +1$: Absurde.) ■

Remark 3.3 The first principle tells : A “material” has an internal energy U , so dU is an exact differential form, and $dU = \alpha + \beta$ is the sum of two differential forms (non exact in general) called the elementary heat $\alpha = \delta Q$ and the elementary work $\beta = \delta W$: Usual notation: $dU = \delta Q + \delta W$. ■

3.2 Curves, paths, trajectories

Definition 3.4 Let Ω be an open subset in E . A (parametric) curve or path in Ω is a function $\vec{r} \in C^1([t_0, t_f]; \Omega)$, where $t_0 < t_f$.

It is a closed when $\vec{r}(t_0) = \vec{r}(t_f)$.

The range, or image, of \vec{r} is $\Gamma = \text{Im} \vec{r} := \{\vec{x} \in E : \exists t \in [t_0, t_f] \text{ s.t. } \vec{x} = \vec{r}(t)\}$ (drawing).

When t is a time, a curve is also called a trajectory, with t_0 and t_f the initial and final times.

Definition 3.5 The tangent vector along \vec{r} at $\vec{x} = \vec{r}(t)$ is $\vec{v}(\vec{x}) := \vec{r}'(t) = \sum_{i=1}^n r_i'(t) \vec{e}_i \in E$. Hence $\vec{r}'(t) = \lim_{h \rightarrow 0} \frac{\vec{r}(t+h) - \vec{r}(t)}{h} = \vec{v}(\vec{r}(t))$ is tangent at $\text{Im} \vec{r}$ at $\vec{r}(t)$. If t is a time and \vec{x} a point in our usual geometric space \mathbb{R}^3 , then the tangent vector is called the velocity.

Notations: A Cartesian basis (\vec{e}_i) being chosen in E , $[\vec{r}(t)] = \begin{pmatrix} r_1(t) \\ \vdots \\ r_n(t) \end{pmatrix}$ and $[\vec{r}'(t)] = \begin{pmatrix} r_1'(t) \\ \vdots \\ r_n'(t) \end{pmatrix}$ mean $\vec{r}(t) = \sum_{i=1}^n r_i(t) \vec{e}_i$ and $\vec{r}'(t) = \sum_{i=1}^n r_i'(t) \vec{e}_i$.

Example 3.6 \mathbb{R}^2 , (\vec{e}_i) Euclidean basis, $\vec{r}: [0, 2\pi] \rightarrow \mathbb{R}^2$ given by $[\vec{r}(t)] = \begin{pmatrix} x = r_1(t) = a + R \cos t \\ y = r_2(t) = b + R \sin t \end{pmatrix}$: Its range: $\text{Im} \vec{r} =$ radius R circle centered at (a, b) , and $[\vec{r}'(t)] = \begin{pmatrix} -R \sin t \\ R \cos t \end{pmatrix}$ (tangent vector at $\vec{r}(t)$). ■

3.3 Integration of a differential form

Let $\vec{r}: [t_0, t_f] \rightarrow \Omega$ be a curve in Ω open set in \mathbb{R}^n .

Definition 3.7 If $\alpha: \Omega \rightarrow E^*$ is a C^0 differential form, then its integral along \vec{r} is the real

$$\int_{\vec{r}} \alpha := \int_{t=t_0}^{t_f} \alpha(\vec{r}(t)) \cdot \vec{r}'(t) dt \stackrel{\text{noted}}{=} \int \alpha \cdot d\vec{r}. \quad (3.3)$$

Example 3.8 $[\alpha(x, y)] = (-y \ x)$ (example 3.2), $[\vec{r}(t)] = \begin{pmatrix} x = R \cos t \\ y = R \sin t \end{pmatrix}$, so $[\vec{r}'(t)] = \begin{pmatrix} -R \sin t \\ R \cos t \end{pmatrix}$, with $t \in [0, 2\pi]$. Thus

$$\int_{\vec{r}} \alpha = \int_{t=t_0}^{t_f} \alpha(\vec{r}(t)) \cdot \vec{r}'(t) dt = \int_{t=0}^{2\pi} R^2 dt = 2\pi R^2 \quad (3.4)$$

since $\alpha(\vec{r}(t)) \cdot \vec{r}'(t) = (-R \sin t \ R \cos t) \cdot \begin{pmatrix} -R \sin t \\ R \cos t \end{pmatrix} = R^2 \sin^2 t + R^2 \cos^2 t = R^2$. ■

Proposition 3.9 If the differential form α is exact, $\alpha = d\phi$ then $\int_{\vec{r}} \alpha$ only depends on the ends of the curve \vec{r} :

$$\int_{\vec{r}} \alpha = \int_{\vec{r}} d\phi = \phi(\vec{r}(t_f)) - \phi(\vec{r}(t_0)) \quad (3.5)$$

(And then we say that « ϕ is a primitive of $\alpha = d\phi$ ».) In particular, if \vec{r} is closed then $\oint_{\vec{r}} d\phi = 0$.

Proof. $(\phi \circ \vec{r})(t) = \phi(\vec{r}(t)) = \phi(r_1(t), \dots, r_n(t))$ gives

$$(\phi \circ \vec{r})'(t) = d\phi(\vec{r}(t)) \cdot \vec{r}'(t) \quad (= \frac{\partial \phi}{\partial x_1}(\vec{r}(t)) \frac{dr_1}{dt}(t) + \dots + \frac{\partial \phi}{\partial x_n}(\vec{r}(t)) \frac{dr_n}{dt}(t)),$$

thus

$$\int_{\vec{r}} d\phi \stackrel{(3.3)}{=} \int_{t_0}^{t_f} d\phi(\vec{r}(t)) \cdot \vec{r}'(t) dt = \int_{t_0}^{t_f} (\phi \circ \vec{r})'(t) dt = [(\phi \circ \vec{r})(t)]_{t_0}^{t_f} = \phi(\vec{r}(t_f)) - \phi(\vec{r}(t_0)).$$

And \vec{r} is closed iff $\vec{r}(t_f) = \vec{r}(t_0)$. ▀

Remark 3.10 Continuation of remark 3.3: $dU = \delta Q + \delta W$ with $\vec{x} = \vec{r}(t_f)$ and $\vec{x}_0 = \vec{r}(t_0)$.

- $dU(\vec{x})$, $\delta Q(\vec{x})$ and $\delta W(\vec{x})$ are meaningful: They are differential forms at a point.
- $U(\vec{x})$ is meaningful (potential at \vec{x}): $U(\vec{x}) = U(\vec{x}_0) + \int_{\vec{r}} dU$.
- But $Q(\vec{x})$ et $W(\vec{x})$ are meaningless; Only $Q(\vec{r}) := \int_{\vec{r}} \delta Q$ and $W(\vec{r}) := \int_{\vec{r}} \delta W$ are meaningful (quantities which depend on a trajectory). So $\int_{\vec{r}} \delta W$ makes sense while $W(\vec{x}) = W(x_0) + \int_{\vec{r}} \delta W$ doesn't make sense: E.g. take $\delta W = \alpha$ in (3.4) which gives that $\int_{\vec{r}} \delta W$ depends on R . We say that Q and W are “quantities of energy” while U is an energy. ▀

4 Issue: Impossible gradient vector

4.1 Linear form and inner scalar product: Riesz representation vector

Let $(\cdot, \cdot)_g$ is a an inner scalar product in a vector space E and $\|\cdot\|_g = \sqrt{(\cdot, \cdot)_g}$ (associated norm), and suppose that E is complete with respect to $\|\cdot\|_g$, so $(E, (\cdot, \cdot)_g)$ is a Hilbert space (always true if $\dim E < \infty$).

Theorem 4.1 (Riesz representation theorem) Let $\ell \in E^*$ be continuous (always true if $\dim E < \infty$). Then ℓ can be represented by a $(\cdot, \cdot)_g$ dependent vector $\vec{\ell}_g \in E$:

$$\forall \ell \in E^*, \exists \vec{\ell}_g \in E \text{ s.t., } \forall \vec{v} \in E, \ell \cdot \vec{v} = (\vec{\ell}_g, \vec{v})_g. \quad (4.1)$$

Proof. Let $\text{Ker } \ell = \{\vec{v} \in E : \ell \cdot \vec{v} = 0\} = \ell^{-1}(0)$ (closed hyperplane since ℓ is continuous). Let $\text{Ker } \ell^\perp = \{\vec{w} \in E : \forall \vec{v}_0 \in \text{Ker } \ell, (\vec{w}, \vec{v}_0)_g = 0\}$ the $(\cdot, \cdot)_g$ -orthogonal space. So $E = \text{Ker } \ell \oplus \text{Ker } \ell^\perp$. Suppose $\ell \neq 0$ (if $\ell = 0$ then $\vec{\ell}_g = \vec{0}$), thus $\exists \vec{w} \notin \text{Ker } \ell$. Call \vec{w}_0 the $(\cdot, \cdot)_g$ -orthogonal projection of \vec{w} on $\text{Ker } \ell$ (drawing). Let $\vec{n} := \frac{\vec{w} - \vec{w}_0}{\|\vec{w} - \vec{w}_0\|_g}$, so $\vec{n} \in \text{Ker } \ell^\perp$ and is $(\cdot, \cdot)_g$ -unitary. Let $\vec{v} \in E$, $\vec{v} = \vec{v}_0 + \lambda \vec{n} \in \text{Ker } \ell \oplus \text{Ker } \ell^\perp$. Thus $(\vec{v}, \vec{n})_g = 0 + \lambda = \lambda$, and thus $\ell(\vec{v}) = 0 + \lambda \ell(\vec{n}) = (\vec{v}, \vec{n})_g \ell(\vec{n}) = (\vec{v}, (\ell \cdot \vec{n}) \vec{n})_g$, thus $\vec{\ell}_g = (\ell \cdot \vec{n}) \vec{n}$ (uniqueness). And (existence) $\vec{\ell}_g := (\ell \cdot \vec{n}) \vec{n}$ trivially satisfies $\ell \cdot \vec{v} = (\vec{\ell}_g, \vec{v})_g$. since $(\vec{\ell}_g, \vec{v}_0)_g = \ell \cdot \vec{v}_0 = 0$ for all $\vec{v}_0 \in \text{Ker } \ell$. Drawing: $\vec{\ell}_g$ is parallel to \vec{n} (is $(\cdot, \cdot)_g$ -orthogonal to $\text{Ker } \ell$). Dependence on $(\cdot, \cdot)_g$: E.g. if $(\cdot, \cdot)_h = 2(\cdot, \cdot)_g$ then $(\vec{\ell}_g, \vec{v})_g = \ell(\vec{v}) = (\vec{\ell}_h, \vec{v})_h = 2(\vec{\ell}_h, \vec{v})_h$ for all \vec{v} , thus $\vec{\ell}_g = 2\vec{\ell}_h \neq \vec{\ell}_h$ (when $\ell \neq 0$). ▀

Dimension calculus: (4.1) gives $\{\ell\}\{\vec{v}\} = \{g\}\{\vec{\ell}_g\}\{\vec{v}\} \stackrel{(1.3)}{=} \{\ell\}^2 \{\vec{\ell}_g\}\{\vec{v}\}$, thus $\{\ell\} = \frac{1}{\{\ell\}}$ as expected: $\vec{\ell}_g \in E$ (“contravariant”), hence its dimension is the inverse of the dimension $\ell \in E^*$ (“covariant”), cf. (1.2).

Remark 4.2 The work done by a differential form α along a path \vec{r} is $W^*(\alpha, \vec{r}) = \int \alpha \cdot d\vec{r}$. And the Riesz representation theorem tells that $\alpha(\vec{x}) \in E^*$ can be represented its $(\cdot, \cdot)_g$ -Riesz representation vector $\vec{\alpha}_g(\vec{x}) \stackrel{\text{noted}}{=} \vec{f}(\vec{x})$ called a “force vector” ($(\cdot, \cdot)_g$ -dependent), thus, with $(\vec{v}, \vec{w})_g \stackrel{\text{noted}}{=} \vec{v} \cdot \vec{w}$,

$$W^*(\alpha, \vec{r}) = \int \alpha \cdot d\vec{r} = \int_{t=t_0}^{t_f} \alpha(\vec{r}(t)) \cdot \vec{r}'(t) dt = \int_{t=t_0}^{t_f} \vec{f}(\vec{r}(t)) \cdot \vec{r}'(t) dt \stackrel{\text{noted}}{=} \int \vec{f} \cdot d\vec{r} \stackrel{\text{noted}}{=} W(\vec{f}, \vec{r}), \quad (4.2)$$

and $W(\vec{f}, \vec{r})$ is called the work of \vec{f} along \vec{r} (fundamental in mechanics). ▀

4.2 Definition of a gradient

Definition 4.3 If $f : E \rightarrow \mathbb{R}$ is C^1 and $\vec{x} \in E$, then the $(\cdot, \cdot)_g$ -Riesz-representation vector of $df(\vec{x})$ is called the $(\cdot, \cdot)_g$ -gradient vector of f at \vec{x} and written $\vec{\nabla}_g f(\vec{x})$ (depends on $(\cdot, \cdot)_g$). So, cf. (4.1),

$$\forall \vec{v} \in E, df(\vec{x}) \cdot \vec{v} = (\vec{\nabla}_g f(\vec{x}), \vec{v})_g. \quad (4.3)$$

If a $(\cdot, \cdot)_g$ is imposed to all and $(\vec{v}, \vec{w})_g \stackrel{\text{noted}}{=} \vec{v} \cdot \vec{w}$, then $\vec{\nabla}_g f \stackrel{\text{noted}}{=} \vec{\nabla} f$, and $df(\vec{x}) \cdot \vec{v} = \vec{\nabla} f(\vec{x}) \cdot \vec{v}$.

4.3 The \mathbb{R}^n space of thermodynamic variables and impossible gradient

E.g. with the thermodynamical variables T, P : The considered Cartesian space is $\mathbb{R}^2 = \mathbb{R} \times \mathbb{R} = \{(T, P)\}$ physically made of the “totally different spaces \mathbb{R} ”: The dimensions of a temperature T and of a pressure P are not comparable. Then choose a Cartesian basis $\vec{e}_1 = (1, 0)$, $\vec{e}_2 = (0, 1)$, where e.g. “1” means 1 Kelvin for \vec{e}_1 , and 1 Pascal for \vec{e}_2 .

Issue: There is no physically meaningful inner scalar product $(\cdot, \cdot)_g$ in this \mathbb{R}^2 : E.g. $\vec{v} = T\vec{e}_1 + P\vec{e}_2$ would give $\|\vec{v}\|^2 = T^2 + P^2 \dots$ which adds a (squared) temperature with a (squared) pressure: Absurd.

Consequence: E.g. for the internal energy function $U : (T, P) \in \mathbb{R}^2 \rightarrow U(T, P) \in \mathbb{R}$ we cannot use the gradient of U , because there is no meaningful inner scalar product in the space $\mathbb{R}^2 = \{(T, P)\}$.

Result: We have to do with (we can only use) the differential dU (not some gradient of U).

5 Thermodynamic: vocabulary

5.1 Thermodynamic variables and functions

Let $[t_0, t_f] \subset \mathbb{R}$ be a time interval, and \mathcal{O} be an open set in the geometric space $\mathbb{R}^3 = \{\vec{x} = (x, y, z)\}$.

Definition 5.1 A thermodynamic function is a function $X_i : \left\{ \begin{array}{l} [t_0, t_f] \times \mathcal{O} \rightarrow \mathbb{R} \\ (t, \vec{x}) \rightarrow X_i(t, \vec{x}), \end{array} \right\}$ that describes a “thermodynamic system”. E.g. X_i =: temperature T , pressure P , volume V , number n of moles, chemical potential μ , internal energy U , entropy S , number N of particles, ... And $\vec{X} = (X_1, \dots, X_n) : [t_0, t_f] \times \mathcal{O} \rightarrow \mathbb{R}^n$ is the associated vector. E.g. $n=2$ and $\vec{X} = (T, P)$.

Definition 5.2 A thermodynamic function X_i will also be called a “thermodynamic variable” when it is “a variable of a thermodynamic function”; E.g. writing $T = \tilde{T}(P, V)$ means that T depends on P and V : Here P and V are the “thermodynamic variables” of the “thermodynamic function” \tilde{T} .

Reminder: For a gaz, the amount of matter is given in moles: One mole is equal to the number of atoms in 12 grams of carbon-12, so one mole = $6.02214076 \cdot 10^{23}$ atoms = Avogadro constant ($\simeq 6.0 \cdot 10^{23}$).

5.2 System in equilibrium and quasi-static transformation

Definition 5.3 A system is in equilibrium iff the thermodynamic functions X_i are uniform in space, i.e.

$$X_i(t, \vec{x}) = X_i(t, \vec{y}), \quad \forall i \in [1, n]_{\mathbb{N}}, \quad t \in [t_0, t_f], \quad \vec{x}, \vec{y} \in \mathcal{O}, \quad \text{and then} \quad X_i(t, \vec{x}) \stackrel{\text{noted}}{=} X_i(t). \quad (5.1)$$

Then the thermodynamic transformation (the trajectory) $t \rightarrow \vec{X}(t)$ is called quasi-static if \vec{X} is C^1 in t ; And then the X_i are called state variables and \vec{X} a state vector. (So, a quasi-static transformation is “slow enough” for the thermodynamic variables to be uniform and C^1 in t .)

In the following, all the transformations will be assumed to be quasi-static.

5.3 State function (“grandeur d’état”)

Definition 5.4 A state function (“grandeur d’état” in French) is a function

$$\phi : \left\{ \begin{array}{l} \mathbb{R}^n \rightarrow \mathbb{R}, \\ \vec{X} \rightarrow \phi(\vec{X}), \end{array} \right. \quad (5.2)$$

where here \mathbb{R}^n is the name for the space of the state variables. E.g. the “internal energy” $\phi = \mathcal{U} : (T, P, V) \rightarrow U = \mathcal{U}(T, P, V)$ (here $n=3$, $\vec{X} = (T, P, V)$, and Φ is defined on its definition domain $\subset \mathbb{R}^3$).

A state function is also the name given to a functional (= a function of functions)

$$\phi : \left\{ \begin{array}{l} \mathcal{F}([t_0, t_f]; \mathbb{R}^n) \rightarrow \mathcal{F}([t_0, t_f]; \mathbb{R}) \\ \vec{X} \rightarrow \phi(\vec{X}) := \phi \circ \vec{X}, \quad \text{with} \quad \phi(\vec{X})(t) := (\phi \circ \vec{X})(t) = \phi(\vec{X}(t)). \end{array} \right. \quad (5.3)$$

E.g. $U = \mathcal{U}(T, P, V)(t) = \mathcal{U}(T(t), P(t), V(t)) =$ the internal energy at t .

The state functions ϕ will be supposed C^1 , so, with (5.2),

$$d\phi(\vec{X}) = \frac{\partial\phi}{\partial X_1}(\vec{X}) dX_1 + \dots + \frac{\partial\phi}{\partial X_n}(\vec{X}) dX_n. \quad (5.4)$$

E.g.,

$$d\mathcal{U}(T, P, V) = \frac{\partial\mathcal{U}}{\partial T}(T, P, V) dT + \frac{\partial\mathcal{U}}{\partial P}(T, P, V) dP + \frac{\partial\mathcal{U}}{\partial V}(T, P, V) dV, \quad (5.5)$$

and thermodynamic notation (shorten notation):

$$dU = \frac{\partial U}{\partial T|_{P,V}} dT + \frac{\partial U}{\partial P|_{T,V}} dP + \frac{\partial U}{\partial V|_{T,P}} dV, \quad (5.6)$$

which in particular tells that here the chosen variables are T, P, V .

5.4 State equation (state law)

Definition 5.5 A state equation (or state law) is an implicit relation between the state variables: It is

$$Z(\vec{X}) = 0, \quad \text{i.e.} \quad Z(T, P, V, \dots) = 0, \quad (5.7)$$

where $Z : \vec{X} \rightarrow Z(\vec{X}) \in \mathbb{R}$ is some function (given by thermodynamic engineers).

Example 5.6 Perfect gas: $Z(T, P, V, n) = PV - nRT$ gives the state equation $PV - nRT = 0$, or the state law $PV = nRT$, where $\vec{X} = (T, P, V, n) \in \mathbb{R}^4$ and $R \simeq 8,31 \text{ J.K}^{-1}.\text{mol}^{-1}$ (perfect gas constant). ■

5.5 Extensive and intensive quantities

Consider a body B , call \mathcal{B} the set of all subsets of B , and consider a function $A : \left\{ \begin{array}{l} \mathcal{B} \rightarrow \mathbb{R}_+ \\ b \rightarrow A(b) \end{array} \right\}$.

Definition 5.7 1. If $A(b_1) + A(b_2) = A(b_1 \cup b_2)$ for all $b_1, b_2 \in \mathcal{B}$, then A is said to be extensive (e.g., volume, number of particles, energy, entropy).

2. If $A(b) = A(B)$ for all $b \in \mathcal{B}$, then A is said to be intensive (e.g., temperature, pressure).

Remark 5.8 Extensivity and intensivity are also defined by: If B is cut in any two equal parts b_1 and b_2 then 1'- A extensive iff $A(b_1) + A(b_2) = A(B)$, and 2'- A intensive iff $A(b_1) = A(b_2) = A(B)$. ■

6 First principle of thermodynamics

6.1 First principle

6.1.1 First part: Existence of an internal energy state function U

Postulate: “the energy cannot be created or destroyed from nothing”, written as

Postulate, first part of the first law:

Any “object” has an “internal energy U ” which is C^1 for any quasi-static transformation.

I.e.: There exists a C^1 function $\mathcal{U} : \vec{X} = (T, P, V, n, \dots) \in \mathbb{R}^n \rightarrow U = \mathcal{U}(\vec{X}) \in \mathbb{R}$ called the internal energy function (with U the value of the internal energy at \vec{X}), s.t. $\mathcal{U} \circ \vec{X} : t \in [t_0, t_f] \rightarrow \mathcal{U}(\vec{X}(t))$ is C^1 for all quasi-static transformation $\vec{X} : t \in [t_0, t_f] \rightarrow \vec{X}(t) \in \mathbb{R}^n$.

6.1.2 Second part: $\Delta U = Q + W$

Observation: The heat Q measured in calories and the work W measured in Joule are energies (with 1 calorie $\simeq 4.184$ Joule). E.g., a friction, due to some work, produces heat. E.g., heating a gas creates an increase in pressure which can produce some work (steam machines).

Postulate, second part of the first law: 1- Along any thermodynamical transformation, the internal energy U received by a body is the sum of the heat Q received and the work W received:

$$\Delta U = Q + W. \quad (6.1)$$

2- And the heat and work are integrals of differential forms δQ and δW (non exact in general).

So, at any point of any quasi-static transformation $\vec{r}: [t_0, t_f] \rightarrow \mathbb{R}^n$,

$$dU = \delta Q + \delta W, \quad (6.2)$$

and

$$\Delta U = \int_{\vec{r}} \delta Q + \int_{\vec{r}} \delta W \stackrel{\text{noted}}{=} Q(\vec{r}) + W(\vec{r}), \quad (6.3)$$

which means $\mathcal{U}(\vec{r}(t_f)) - \mathcal{U}(\vec{r}(t_0)) = \int_{t_0}^{t_f} \delta Q(\vec{r}(t)) \cdot \vec{r}'(t) dt + \int_{t_0}^{t_f} \delta W(\vec{r}(t)) \cdot \vec{r}'(t) dt$.

Remark 6.1 “Heat” and “work” are immaterial quantities (no “exchange of matter”); They are locally mathematically modeled by a differential forms at a point along a trajectory, only after a trajectory \vec{r} has been considered (δQ and δW don’t exist if there is no transformation). In other words, heat and work are not a characteristic of a body: They only exists temporarily. (And heat can only be exchanged spontaneously from a hot body to a cold body; This irreversibility is the object of the second law.) ■■

6.1.3 Third part : U is an extensive quantity

Postulate, third part of the first law of thermodynamics

« The internal energy U is an extensive quantity. »

So the energy of two joined systems is the sum of the two energies.

6.2 Some applications

6.2.1 C_V the thermal capacity at constant volume

Goal: Quantify the rate of heat $\frac{\delta Q}{\delta T}$, when heating a closed system at constant volume.

Hypotheses: • The number n of moles is constant (closed system), and the thermodynamical variables are T, P, V ; So $\vec{X} = (T, P, V)$.

• Isochoric transformation (e.g. bicycle pump, static piston, and we heat), i.e., at all time,

$$V = V_0 \quad (6.4)$$

so the (thermodynamical) variables left are T, P .

• (We heat and) P depends on T , i.e. $\exists \tilde{P}_{V_0} \in C^1(\mathbb{R}; \mathbb{R})$ s.t.

$$P = \tilde{P}_{V_0}(T). \quad (6.5)$$

Thus the isochoric transformation only depends on the temperature, i.e. is of the type

$$\vec{\gamma}_{V_0} : \left\{ \begin{array}{l} [T_1, T_2] \rightarrow \mathbb{R}^3 \\ T \rightarrow \vec{X} = \vec{\gamma}_{V_0}(T) = (T, \tilde{P}_{V_0}(T), V_0) \end{array} \right\}, \quad \text{so} \quad [\vec{\gamma}_{V_0}(T)] = \begin{pmatrix} T \\ \tilde{P}_{V_0}(T) \\ V_0 \end{pmatrix}. \quad (6.6)$$

• The only elementary work considered is $\delta W = -P dV$. So here $\delta W = 0$ (isochoric), thus

$$d\mathcal{U} = \delta Q \quad \text{along } \vec{\gamma}_{V_0}. \quad (6.7)$$

Definition 6.2 The thermal capacity per mole at constant volume $V = V_0$ at $\vec{X} = \vec{\gamma}_{V_0}(T)$ is

$$C_{V_0}(\vec{X}) := \frac{1}{n} \lim_{\Delta T \rightarrow 0} \frac{\Delta Q}{\Delta T} \quad \text{along } \vec{\gamma}_{V_0}. \quad (6.8)$$

Question: What does it mean? (Q is not a function defined at points but at trajectories.)

Answer: The considered thermodynamic transformation is $\vec{\gamma}_{V_0}$, so

$$nC_{V_0} \stackrel{(6.7)}{=} \lim_{\Delta T \rightarrow 0} \frac{\Delta U}{\Delta T} \text{ along } \vec{\gamma}_{V_0}, \quad \text{i.e.} \quad nC_{V_0}(\vec{\gamma}_{V_0}(T)) = \lim_{h \rightarrow 0} \frac{U(\vec{\gamma}_{V_0}(T+h)) - U(\vec{\gamma}_{V_0}(T))}{h}, \quad (6.9)$$

so

$$nC_{V_0}(\vec{\gamma}_{V_0}(T)) = \frac{d(\mathcal{U} \circ \vec{\gamma}_{V_0})}{dT}(T) = d\mathcal{U}(\vec{\gamma}_{V_0}(T)) \cdot \vec{\gamma}_{V_0}'(T) = [d\mathcal{U}(\vec{\gamma}_{V_0}(T))] \cdot [\vec{\gamma}_{V_0}'(T)]. \quad (6.10)$$

Calculation: $[d\mathcal{U}] = \left(\frac{\partial \mathcal{U}}{\partial T} \quad \frac{\partial \mathcal{U}}{\partial P} \quad \frac{\partial \mathcal{U}}{\partial V} \right)$ and $[\vec{\gamma}_{V_0}'(T)] \stackrel{(6.6)}{=} \begin{pmatrix} 1 \\ \tilde{\mathcal{P}}_{V_0}'(T) \\ 0 \end{pmatrix}$ give

$$nC_{V_0}(\vec{X}) = \frac{\partial \mathcal{U}}{\partial T}(\vec{X}) + \frac{\partial \mathcal{U}}{\partial P}(\vec{X}) \tilde{\mathcal{P}}_{V_0}'(T) + 0 \quad \text{at } \vec{X} = \vec{\gamma}_{V_0}(t). \quad (6.11)$$

Thermodynamic notations:

$$nC_V dT = dU \quad \text{along } \vec{\gamma}_V, \quad \text{and} \quad nC_V = \frac{\partial U}{\partial T}|_{P,V} + \frac{\partial U}{\partial P}|_{T,V} \frac{\partial P}{\partial T}|_V \quad \text{along } \vec{\gamma}_V. \quad (6.12)$$

And $\delta Q = dU$ along $\vec{\gamma}_{V_0}$ gives $\int_{\vec{\gamma}_{V_0}} \delta Q = \int_{\vec{\gamma}_{V_0}} dU$, thus

$$Q(\vec{\gamma}_{V_0}) = \int_{T_1}^{T_2} nC_{V_0}(\vec{\gamma}_{V_0}(T)) dT \quad (= \int_{T_1}^{T_2} dU(\vec{\gamma}_{V_0}(T)) \cdot \vec{\gamma}_{V_0}'(T) dT = \Delta U). \quad (6.13)$$

6.2.2 C_P the thermal capacity at constant pressure

Goal: Quantify the rate of heat $\frac{\delta Q}{\delta T}$, when heating a closed system at constant pressure.

Hypotheses • The number n of moles is constant (closed system), and the thermodynamical variables are T, P, V ; So $\vec{X} = (T, P, V)$.

• Isobaric transformation (e.g., bicycle pump, free piston, and we heat), i.e., at all time,

$$P = P_0, \quad (6.14)$$

so the (thermodynamical) variables left are T, V .

• (We heat and) V depends on T , i.e. $\exists \hat{\mathcal{V}}_{P_0} \in C^1(\mathbb{R}; \mathbb{R})$ s.t.

$$V = \hat{\mathcal{V}}_{P_0}(T). \quad (6.15)$$

Thus the considered thermodynamic transformation is of the type

$$\vec{\gamma}_{P_0} : \left\{ \begin{array}{l} [T_1, T_2] \rightarrow \mathbb{R}^3 \\ T \rightarrow \vec{X} = \vec{\gamma}_{P_0}(T) = (T, P_0, \hat{\mathcal{V}}_{P_0}(T)) \end{array} \right\}, \quad \text{so} \quad [\vec{\gamma}_{P_0}(T)] = \begin{pmatrix} T \\ P_0 \\ \hat{\mathcal{V}}_{P_0}(T) \end{pmatrix}. \quad (6.16)$$

• The only elementary work considered is $\delta W = -P dV$. Thus

$$d\mathcal{U} = \delta Q - P dV \quad \text{along } \vec{\gamma}_{P_0}. \quad (6.17)$$

Definition 6.3 C_{P_0} the thermal capacity per mole at constant pressure $P = P_0$ at $\vec{X} = \vec{\gamma}_{P_0}(T)$ is

$$C_{P_0}(\vec{X}) := \frac{1}{n} \lim_{\Delta T \rightarrow 0} \frac{\Delta Q}{\Delta T} \quad \text{along } \vec{\gamma}_{P_0}. \quad (6.18)$$

Question: What does it mean? (Q is not a function defined at points but at trajectories.)

Answer: Here $\delta Q(\vec{\gamma}_{P_0}(T)) \stackrel{(6.17)}{=} d\mathcal{U}(\vec{\gamma}_{P_0}(T)) + P_0 d\hat{\mathcal{V}}_{P_0}(T)$ along $\vec{\gamma}_{P_0}$, hence (6.18) means

$$nC_{P_0}(\vec{\gamma}_{P_0}(T)) = \lim_{\Delta T \rightarrow 0} \frac{\mathcal{U}(\vec{\gamma}_{P_0}(T + \Delta T)) - \mathcal{U}(\vec{\gamma}_{P_0}(T)) + P_0 \hat{\mathcal{V}}_{P_0}(T + \Delta T) - P_0 \hat{\mathcal{V}}_{P_0}(T)}{\Delta T}. \quad (6.19)$$

Thus

$$nC_{P_0}(\vec{\gamma}_{P_0}(T)) = \frac{d(\mathcal{U} \circ \vec{\gamma}_{P_0})}{dT}(T) + P_0 \hat{\mathcal{V}}_{P_0}'(T) = d\mathcal{U}(\vec{\gamma}_{P_0}(T)) \cdot \vec{\gamma}'(T) + P_0 \hat{\mathcal{V}}_{P_0}'(T). \quad (6.20)$$

Calculation: $[d\mathcal{U}] = \left(\frac{\partial \mathcal{U}}{\partial T} \quad \frac{\partial \mathcal{U}}{\partial P} \quad \frac{\partial \mathcal{U}}{\partial V} \right)$ and $\vec{\gamma}_{P_0}'(T) \stackrel{(6.16)}{=} \begin{pmatrix} 1 \\ 0 \\ \hat{\mathcal{V}}_{P_0}'(T) \end{pmatrix}$ give, at $\vec{X} = \vec{\gamma}_{P_0}(t)$,

$$nC_{P_0}(\vec{X}) = \frac{\partial \mathcal{U}}{\partial T}(\vec{X}) + 0 + \frac{\partial \mathcal{U}}{\partial V}(\vec{X}) \hat{\mathcal{V}}_{P_0}'(T) + P_0 \hat{\mathcal{V}}_{P_0}'(T) \quad \text{along } \vec{\gamma}_{P_0}. \quad (6.21)$$

Thermodynamic notations:

$$nC_P dT = dU + P dV \quad \text{along } \vec{\gamma}_P, \quad \text{and} \quad nC_P = \frac{\partial \mathcal{U}}{\partial T}|_{P,V} + \frac{\partial \mathcal{U}}{\partial V}|_{T,P} \frac{\partial V}{\partial T}|_P + P \frac{\partial V}{\partial T}|_P \quad \text{along } \vec{\gamma}_P. \quad (6.22)$$

And $\delta Q = dU + P dV$ along $\vec{\gamma}_{V_0}$ gives $\int_{\vec{\gamma}_{V_0}} \delta Q = \int_{\vec{\gamma}_{V_0}} dU + P dV$, thus

$$Q(\vec{\gamma}_{P_0}) \stackrel{(6.18)}{=} \int_{T_1}^{T_2} nC_{P_0}(\vec{\gamma}_{P_0}(T)) dT = \int_{T_1}^{T_2} d\mathcal{U}(\vec{\gamma}_{P_0}(T)) \cdot \vec{\gamma}'(T) + P_0 \hat{\mathcal{V}}_{P_0}'(T) dT = \Delta U + P_0 \Delta V. \quad (6.23)$$

6.2.3 C_V vs C_P for a perfect gas, and $\gamma = \frac{C_P}{C_V}$

Joule experiment for perfect gas (approximated by “air at very low pressure”). First result: $U = \mathcal{U}(T, P, V)$ is independent of P and V , so $\frac{\partial \mathcal{U}}{\partial P} = \frac{\partial \mathcal{U}}{\partial V} = 0$. Thus, at $\vec{X} = (T, P, V)$,

$$nC_V(\vec{X}) \stackrel{(6.11)}{=} \frac{\partial \mathcal{U}}{\partial T}(\vec{X}), \quad \text{and} \quad nC_P(\vec{X}) \stackrel{(6.21)}{=} \frac{\partial \mathcal{U}}{\partial T}(\vec{X}) + P \frac{\partial \hat{\mathcal{V}}}{\partial T}(T, P). \quad (6.24)$$

And $V = \hat{\mathcal{V}}(T, P) = \frac{nRT}{P}$, thus $\frac{\partial \hat{\mathcal{V}}}{\partial T}(T, P) = \frac{nR}{P}$, thus $nC_P(\vec{X}) = nC_V(\vec{X}) + nR$.

Second result: C_V et C_P are constant for a perfect gas, i.e. independent of \vec{X} , thus

$$C_P = C_V + R. \quad (6.25)$$

Hence $C_P > C_V$: For an increase ΔT of the temperature, the received heat at constant pressure is greater than the received heat at constant volume.

Definition 6.4 The adiabatic index (ratio of molar heat capacities) is

$$\gamma := \frac{C_P}{C_V} = 1 + \frac{R}{C_V} \quad (> 1). \quad (6.26)$$

(E.g., mono-atomic perfect gas : $\gamma = \frac{5}{3}$, di-atomic perfect gas : $\gamma = \frac{7}{5}$.)

6.2.4 Adiabatic transformation and perfect gas: $PV^\gamma = \text{constant}$

Definition 6.5 A (quasi-static) transformation is adiabatic iff $\delta Q = 0$ (no heat exchange, e.g. with “perfectly” insulated walls).

Observation: Along an adiabatic path neither P or V are constant, but they are linked. How?

Here perfect gas: $T = \frac{PV}{nR} = \tilde{T}(P, V)$ gives $d\tilde{T}(P, V) = \frac{1}{nR}V dP + \frac{1}{nR}P dV$, thus (thermodynamic notations)

$$nC_V dT = nC_V \left(\frac{1}{nR}V dP + \frac{1}{nR}P dV \right) \stackrel{(6.12)}{=} dU. \quad (6.27)$$

And along an adiabatic transform $dU = 0 - P dV$, thus $nC_V \left(\frac{1}{nR}V dP + \frac{1}{nR}P dV \right) = -P dV$; Thus $(1 + \frac{R}{C_V})P dV + V dP = 0$, thus, with $\gamma \stackrel{(6.26)}{=} 1 + \frac{R}{C_V}$,

$$\gamma \frac{dV}{V} + \frac{dP}{P} = 0 \quad \text{along an adiabatic path for a perfect gas.} \quad (6.28)$$

Hence

$$PV^\gamma = c = \text{constant, along an adiabatic path for a perfect gas.} \quad (6.29)$$

Exercise 6.6 Give rigorous steps to get (6.29).

Answer. Consider a trajectory $t \in \rightarrow [\vec{r}(t)] = \begin{pmatrix} T(t) \\ P(t) \\ V(t) \end{pmatrix} \in \mathbb{R}^3$ s.t. $\delta Q(\vec{r}(t)) = 0$ for all t (adiabatic). With $T^{\text{perfect}}_{\text{gas}} \frac{PV}{nR}$ we have $[\vec{r}(t)] = \begin{pmatrix} \frac{P(t)V(t)}{nR} \\ P(t) \\ V(t) \end{pmatrix}$, thus $[\vec{r}'(t)] = \begin{pmatrix} \frac{1}{nR} (V(t)P'(t) + P(t)V'(t)) \\ P'(t) \\ V'(t) \end{pmatrix}$. With (perfect gas) $\frac{\partial \mathcal{U}}{\partial T}(\vec{r}(t)) = nC_V$, $\frac{\partial \mathcal{U}}{\partial P}(\vec{r}(t)) = 0 = \frac{\partial \mathcal{U}}{\partial V}(\vec{r}(t))$. Thus

$$d\mathcal{U}(\vec{r}(t)).\vec{r}'(t) = nC_V \frac{1}{nR} (V(t)P'(t) + P(t)V'(t)) + 0 + 0 \quad \text{along } \vec{r}. \quad (6.30)$$

And, $\delta W(T, P, V) = -P dV$, i.e. $[\delta W(T, P, V)] = (0 \quad 0 \quad -P)$ (row matrix), thus $\delta W(\vec{r}(t)).\vec{r}'(t) = 0 + 0 - P(t)V'(t)$, thus $dU = \delta W$ (adiabatic) gives $dU(\vec{r}(t)).\vec{r}'(t) = \delta W(\vec{r}(t)).\vec{r}'(t)$, hence

$$C_V \left(\frac{V(t)}{R} P'(t) + \frac{P(t)}{R} V'(t) \right) = -P(t)V'(t) \quad \text{along } \vec{r}, \quad (6.31)$$

thus $\gamma \frac{V'(t)}{V(t)} + \frac{P'(t)}{P(t)} = 0$, thus $\gamma \log(V(t)) + \log(P(t)) = \text{constant}$, thus $\log(P(t)V(t)^\gamma) = \text{constant}$, along \vec{r} . \blacksquare

6.2.5 Enthalpy, and constant pressure transformation

Definition 6.7 The enthalpy at a given thermodynamical state is

$$H := U + PV. \quad (6.32)$$

Application: Suppose: • The number n of moles is constant (closed system), • the thermodynamical variables are T, P, V , and • $V = \hat{V}(T, P)$. Thus the enthalpy function $\hat{\mathcal{H}}: \mathbb{R}^2 \rightarrow \mathbb{R}$ is

$$(H =) \quad \hat{\mathcal{H}}(T, P) := \mathcal{U}(T, P, \hat{V}(T, P)) + P \hat{V}(T, P). \quad (6.33)$$

Hence

$$(H =) \quad \hat{\mathcal{H}}(T, P_0) = \mathcal{U}(T, P_0, \hat{V}_{P_0}(T)) + P_0 \hat{V}_{P_0}(T) \quad \text{along } \vec{\gamma}_{P_0}. \quad (6.34)$$

Thus

$$\frac{\partial \hat{\mathcal{H}}}{\partial T}(T, P_0) = \frac{\partial \mathcal{U}}{\partial T}(\vec{X}) + 0 + \frac{\partial \mathcal{U}}{\partial V}(\vec{X}) \hat{V}_{P_0}'(T) + P_0 \hat{V}_{P_0}'(T) \quad \text{at } \vec{X} = \vec{\gamma}_{P_0}(T) = (T, P_0, \hat{V}_{P_0}(T)). \quad (6.35)$$

Thus

$$nC_{P_0}(\vec{X}) \stackrel{(6.21)}{=} \frac{\partial \hat{\mathcal{H}}}{\partial T}(T, P_0) = \text{rate of variation of } H \text{ along } \vec{\gamma}_{P_0} \text{ at } \vec{X} = \vec{\gamma}_{P_0}(T). \quad (6.36)$$

Thermodynamical notation: $nC_P = \frac{\partial H}{\partial T}|_P$.

7 Second principle of thermodynamics

7.1 Introduction: Findings and Clausius and Kelvin postulates

- Heat is transmitted spontaneously from a hot body to a cold body, never the other way around.
- The heat transfer increases with the temperature difference.
- Heat cannot be transformed entirely into work.

Example 7.1 • A mass at the end of a spring in a heat-insulated container: Heat is created (air friction and internal friction in the spring...), but it doesn't spontaneously set the mass in motion.

- Hot water and cold water mix spontaneously to make moderately warm water; But moderately hot water does not spontaneously give hot water on one side and cold water on the other.
- A gas doesn't compress spontaneously (work must be done). \blacksquare

Clausius postulate: "A cold body receives heat from a hot one", or "Heat cannot flow spontaneously from a cold body to a warm body", or

A thermodynamic transformation whose only result is to transfer heat from a body at a given temperature to a body at a higher temperature is impossible.

More precisely: Consider a closed isolated system Z made of two sub-systems Z_1 and Z_2 , call T_{10} and T_{20} their (uniform) initial temperatures, consider a (quasi-static) trajectory $\vec{r}: t \in [t_0, t_0+h] \rightarrow \vec{X} = \vec{r}(t)$ where $h > 0$, and suppose $\delta W = 0$. Postulate: If $T_{10} < T_{20}$ then the heat Q_1 and Q_2 received by Z_1 and Z_2 satisfy

$$Q_1(\vec{r}) > 0 \quad \text{and} \quad Q_2(\vec{r}) < 0. \quad (7.1)$$

Lord Kelvin (William Thomson) postulate:

$$\text{In a constant temperature cyclic transformation, no work can be created.} \quad (7.2)$$

7.2 Second principle

Second principle (Clausius): $\vec{X} = (T, P, V, n, \dots) \in \mathbb{R}^n$ being the thermodynamic vector and the transformations being quasi-static, there exists a function $S \in C^1(\mathbb{R}^n; \mathbb{R})$, called entropy, which is

- a state function,
- extensive,
- for a closed isolated system, S is maximum, and
- with T in Kelvin degree ($T > 0$),

$$dS \geq \frac{\delta Q}{T}, \quad (7.3)$$

i.e. $dS(\vec{X}) \geq \frac{\delta Q(\vec{X})}{T}$. So

$$\Delta S \geq \int_{\vec{r}} \frac{\delta Q}{T} \quad (= \int_{t_0}^{t_f} \frac{\delta Q(\vec{r}(t)) \cdot \vec{r}'(t)}{T(t)} dt) \quad (7.4)$$

where $\Delta S = S(\vec{r}(t_f)) - S(\vec{r}(t_0))$ and $\vec{r}: t \in [t_0, t_f] \rightarrow \vec{X} = \vec{r}(t) \in \mathbb{R}^n$ is a trajectory.

Corollary: For a closed trajectory \vec{r} ,

$$\oint_{\vec{r}} \frac{\delta Q}{T} \leq 0, \quad (7.5)$$

since $\Delta S = 0$ (because S is a state function). In particular, for a closed path at constant temperature, a closed isolated system loses heat (in fact it is the reason for the postulate (7.4)-(7.3)).

Remark 7.2 Any strictly decreasing function $f: T \rightarrow f(T)$ enables to define an entropy $= f(T) \delta Q$ (not only $f(T) = \frac{1}{T}$). But the simple function $f(T) = \frac{1}{T}$ chosen by Clausius enables a simple dimensional analysis, the entropy dimension being Joule.Kelvin⁻¹. ■■

7.3 Reversible transformation

Definition 7.3 A transformation along a path \vec{r} is reversible iff

$$dS = \frac{\delta Q}{T} \text{ along } \vec{r}, \quad \text{i.e.} \quad \Delta S = \int_{\vec{r}} \frac{\delta Q}{T}. \quad (7.6)$$

NB: A reversible transformation does not exist in real life: It can only be approximated.

Example 7.4 $\delta W = -P dV$ gives $\delta Q = dU + P dV$; Thus for a perfect gas ($dU = C_V dT$) and a reversible transformation:

$$dS = \frac{\delta Q}{T} = \frac{C_V}{T} dT + \frac{P}{T} dV = C_V \frac{dT}{T} + nR \frac{dV}{V}, \quad \text{thus} \quad \Delta S = C_V \log \frac{T_f}{T_0} + nR \log \frac{V_f}{V_0} \quad (7.7)$$

when T_0, V_0 and T_f, V_f are the initial and final temperatures and volumes. ■■

7.4 Some applications

Since U and S are now defined, they can also be chosen as thermodynamic variables.

7.4.1 U function of S and V

Consider a C^1 reversible transformation, so $\delta Q = T dS$, and suppose $\delta W = -P dV$. Thus

$$dU = T dS - P dV \quad (\text{thermodynamical notation}). \quad (7.8)$$

Thus it is “natural” to choose S and V as “thermodynamic variables” for U : Define $\bar{U} : \mathbb{R}^2 \rightarrow \mathbb{R}$ by

$$d\bar{U}(S, V) = \bar{T}(S, V) dS - \bar{P}(S, V) dV, \quad \text{i.e.} \quad \frac{\partial \bar{U}}{\partial S}(S, V) = \bar{T}(S, V), \quad \frac{\partial \bar{U}}{\partial V}(S, V) = -\bar{P}(S, V). \quad (7.9)$$

(So $\mathcal{U}(T, P, V) = \bar{U}(S, V)$ at the considered thermodynamic state.) Thermodynamic notations:

$$\frac{\partial U}{\partial S}|_V = T, \quad \frac{\partial U}{\partial V}|_S = -P. \quad (7.10)$$

7.4.2 S as a function of U and V

Consider a C^1 reversible transformation, so $\delta Q = T dS$, and suppose $\delta W = -P dV$. Thus (7.8) gives

$$dS = \frac{1}{T} dU + \frac{P}{T} dV \quad (\text{thermodynamical notation}). \quad (7.11)$$

Thus it is “natural” to choose U and V as “thermodynamic variables” for S : Define $\underline{S} : \mathbb{R}^2 \rightarrow \mathbb{R}$ by

$$d\underline{S}(U, V) = \frac{1}{\underline{T}(U, V)} dU + \frac{\underline{P}(U, V)}{\underline{T}(U, V)} dV, \quad \text{i.e.} \quad \frac{\partial \underline{S}}{\partial U}(U, V) = \frac{1}{\underline{T}(U, V)}, \quad \frac{\partial \underline{S}}{\partial V}(U, V) = \frac{\underline{P}(U, V)}{\underline{T}(U, V)}. \quad (7.12)$$

Thermodynamic notations:

$$\frac{\partial S}{\partial U}|_V = \frac{1}{T} \quad \text{and} \quad \frac{\partial S}{\partial V}|_U = \frac{P}{T}. \quad (7.13)$$

Remark. Fix $V = V_0$ and write $S = \underline{S}(U, V_0) = \underline{S}_{V_0}(U)$ and $U = \bar{U}(S, V_0) = \bar{U}_{V_0}(S)$. So $\underline{S}_{V_0} = \bar{U}_{V_0}^{-1}$ (reversible case): This is a change of variables $U \leftrightarrow S$ at constant volume.

7.5 Irreversible transformation and created entropy

Definition 7.5 An irreversible transformation is a transformation along a path \vec{r} s.t.

$$(\mathcal{S}_2 - \mathcal{S}_1) - \Delta S > \int_{\vec{r}} \frac{\delta Q}{T}. \quad (7.14)$$

The elementary created entropy is $\delta \mathcal{S}_{\text{created}} = dS - \frac{\delta Q}{T}$, and the created entropy along \vec{r} is

$$\int_{\vec{r}} \delta \mathcal{S}_{\text{created}} := \Delta S - \int_{\vec{r}} \frac{\delta Q}{T}. \quad (7.15)$$

8 Enthalpy, free energy, free enthalpy

8.1 Enthalpy $H = U + PV$ with variables S and P

For the enthalpy ($H = U + PV$ at some thermodynamical state cf. (6.33)), choose the thermodynamical variables to be S and P , i.e. consider the enthalpy function $\hat{\mathcal{H}} : \mathbb{R}^2 \rightarrow \mathbb{R}$ defined by

$$(H =) \quad \hat{\mathcal{H}}(S, P) = \hat{\mathcal{U}}(S, P) + P \hat{\mathcal{V}}(S, P). \quad (8.1)$$

Proposition 8.1 With $\delta W = -P dV$ and for a reversible transformation, we have

$$d\hat{\mathcal{H}}(S, P) = \hat{\mathcal{T}}(S, P) dS + \hat{\mathcal{V}}(S, P) dP, \quad \text{i.e.} \quad \frac{\partial \hat{\mathcal{H}}}{\partial S}(S, P) = \hat{\mathcal{T}}(S, P), \quad \frac{\partial \hat{\mathcal{H}}}{\partial P}(S, P) = \hat{\mathcal{V}}(S, P), \quad (8.2)$$

Thermodynamic notations (reversible transformation):

$$dH = T dS + V dP, \quad \text{i.e.} \quad \frac{\partial H}{\partial S}|_P = T, \quad \frac{\partial H}{\partial P}|_S = V, \quad (8.3)$$

Proof. In (8.1), $U = \widehat{\mathcal{U}}(S, P) = \overline{\mathcal{U}}(S, V) = \overline{\mathcal{U}}(S, \widehat{\mathcal{V}}(S, P))$, with $T = \overline{\mathcal{T}}(S, V) = \frac{\partial \overline{\mathcal{U}}}{\partial S}(S, V)$ and $P = \overline{\mathcal{P}}(S, V) = -\frac{\partial \overline{\mathcal{U}}}{\partial V}(S, V)$, cf. (7.9). Thus

$$\begin{cases} \frac{\partial \widehat{\mathcal{U}}}{\partial S}(S, P) = \frac{\partial \overline{\mathcal{U}}}{\partial S}(S, \widehat{\mathcal{V}}(S, P)) + \frac{\partial \overline{\mathcal{U}}}{\partial V}(S, \widehat{\mathcal{V}}(S, P)) \frac{\partial \widehat{\mathcal{V}}}{\partial S}(S, P) = T - P \frac{\partial \widehat{\mathcal{V}}}{\partial S}(S, P), \\ \frac{\partial \widehat{\mathcal{U}}}{\partial P}(S, P) = \frac{\partial \overline{\mathcal{U}}}{\partial V}(S, \widehat{\mathcal{V}}(S, P)) \frac{\partial \widehat{\mathcal{V}}}{\partial P}(S, P) = -P \frac{\partial \widehat{\mathcal{V}}}{\partial P}(S, P). \end{cases} \quad (8.4)$$

Thus $H \stackrel{(8.1)}{=} \widehat{\mathcal{H}}(S, P) = \widehat{\mathcal{U}}(S, P) + P \widehat{\mathcal{V}}(S, P)$ gives

$$\begin{cases} \frac{\partial \widehat{\mathcal{H}}}{\partial S}(S, P) = \frac{\partial \widehat{\mathcal{U}}}{\partial S}(S, P) + P \frac{\partial \widehat{\mathcal{V}}}{\partial S}(S, P) = T = \widehat{\mathcal{T}}(S, P), \\ \frac{\partial \widehat{\mathcal{H}}}{\partial P}(S, P) = \frac{\partial \widehat{\mathcal{U}}}{\partial P}(S, P) + \widehat{\mathcal{V}}(S, P) + P \frac{\partial \widehat{\mathcal{V}}}{\partial P}(S, P) = \widehat{\mathcal{V}}(S, P). \end{cases} \quad (8.5)$$

■

Exercise 8.2 Prove that the change of variable $T \leftrightarrow S$ implicitly used to obtain $\widehat{\mathcal{H}}(S, P)$ from $\widehat{\mathcal{H}}(T, P)$, cf. (6.33), is in fact a Legendre transform.

Answer. $U = \overline{\mathcal{U}}(S, V) = \widehat{\mathcal{U}}(S, P)$ gives $\overline{\mathcal{U}}_S(V) = \widehat{\mathcal{U}}_S(P)$ at any given S , so P is necessarily a function of V . In fact, $P \stackrel{(7.9)}{=} -\frac{\partial \overline{\mathcal{U}}}{\partial V}(S, V) = \overline{\mathcal{P}}(S, V) = \overline{\mathcal{P}}_S(V)$, thus

$$P = -\overline{\mathcal{U}}_S'(V) = \text{the slope of } \overline{\mathcal{U}}_S \text{ (up to the sign)} \quad (8.6)$$

which is what the Legendre transform does (when $\overline{\mathcal{U}}_S$ is strictly convex). ■

8.2 Free energy $F = U - TS$ (variables T and V)

The free energy F is (at a given thermodynamical state)

$$F = U - TS, \quad \text{so, formally,} \quad dF = dU - T dS - S dT. \quad (8.7)$$

And with $\delta W = -P dV$ and a reversible transformation, $dU = T dS - P dV$, thus

$$dF = -S dT - P dV, \quad (8.8)$$

and the “natural” variables are T and V : Define the free energy function $\tilde{F} : \mathbb{R}^2 \rightarrow \mathbb{R}$ by

$$d\tilde{F}(T, V) = -\tilde{S}(T, V) dT - \tilde{P}(T, V) dV, \quad \text{i.e.} \quad \frac{\partial \tilde{F}}{\partial T}(T, V) = -\tilde{S}(T, V), \quad \frac{\partial \tilde{F}}{\partial V}(T, V) = -\tilde{P}(T, V). \quad (8.9)$$

Thermodynamic notation (reversible transformation): $F = U - TS$ with

$$dF = -S dT - P dV, \quad \text{i.e.} \quad \frac{\partial F}{\partial T}|_V = -S, \quad \frac{\partial F}{\partial V}|_T = -P. \quad (8.10)$$

Interpretation: For a reversible transformation at constant temperature:

$$dF = 0 - P dV = \delta W \quad \text{at constant temperature,} \quad (8.11)$$

so F is the energy available as work at constant temperature (for a reversible transformation).

Exercise 8.3 With $\delta W = -P dV$ and a reversible transformation, express F with the Legendre transform $S \rightarrow T = \overline{\mathcal{U}}'_V(S)$ (slope of $\overline{\mathcal{U}}_V$ at S). And get (8.9).

Answer. $dU = T dS - P dV$, so

$$d\overline{\mathcal{U}}(S, V) = \overline{\mathcal{T}}(S, V) dS - \overline{\mathcal{P}}(S, V) dV. \quad (8.12)$$

Thus $F = U - TS$ reads $F = \overline{F}(S, V) = \overline{\mathcal{U}}(S, V) - \overline{\mathcal{T}}(S, V)S$ (value at the considered thermodynamical state), with $F = \tilde{F}(T, V) = \overline{F}(S, V)$, thus $\tilde{F}_V(T) = \overline{F}_V(S)$ at any V : This is a change of variable $T \leftrightarrow S$, given by

$$T \stackrel{(7.9)}{=} \frac{\partial \overline{\mathcal{U}}}{\partial S}(S, V) = \overline{\mathcal{U}}'_V(S) = \text{slope of } \overline{\mathcal{U}}_V \text{ at } S: \text{Legendre transform.} \quad (8.13)$$

Then $U = \tilde{\mathcal{U}}_V(T) = \overline{\mathcal{U}}_V(S)$ gives $\tilde{\mathcal{U}}_V(T) = \overline{\mathcal{U}}_V(\tilde{S}_V(T))$. Thus $F_V = \overline{F}(S) = \tilde{F}_V(T)$ when $T = T_V(S) = \overline{\mathcal{U}}'_V(S)$, thus $\overline{F}_V(S) = \tilde{F}_V(T)$ is a Legendre transform, at any V .

Then $\tilde{F}(T, V) = \tilde{U}(T, V) - T\tilde{S}(T, V) = \bar{U}(S(T, V), V) - T\tilde{S}(T, V)$ gives

$$\begin{cases} \frac{\partial \tilde{F}}{\partial T}(T, V) = \frac{\partial \bar{U}}{\partial S}(\tilde{S}(T, V), V) \frac{\partial \tilde{S}}{\partial T}(T, V) - \tilde{S}(T, V) - T \frac{\partial \tilde{S}}{\partial T}(T, V) \stackrel{(8.13)}{=} -\tilde{S}(T, V), \\ \frac{\partial \tilde{F}}{\partial V}(T, V) = \frac{\partial \bar{U}}{\partial S}(\tilde{S}(T, V), V) \frac{\partial \tilde{S}}{\partial V}(T, V) + \frac{\partial \bar{U}}{\partial V}(\tilde{S}(T, V), V) - T \frac{\partial \tilde{S}}{\partial V}(T, V) \stackrel{(8.13)}{=} \frac{\partial \bar{U}}{\partial V}(\tilde{S}(T, V), V). \end{cases} \quad (8.14)$$

And $P \stackrel{(7.9)}{=} -\frac{\partial \bar{U}}{\partial V}(S, V) = \bar{P}(S, V) = \bar{P}(\tilde{S}(T, V), V) = \tilde{P}(T, V)$, thus (8.9). \blacksquare

8.3 Free enthalpy $G = H - TS$ (Gibbs energy, variables T and P)

The free enthalpy G is

$$G := H - TS \quad (= U + PV - TS). \quad (8.15)$$

With $\delta W = -P dV$ and a reversible transformation, $dU = T dS - P dV$, thus (formally)

$$\begin{aligned} dG &= (T dS - P dV) + (V dP + P dV) - (S dT + T dS) \\ &= V dP - S dT, \end{aligned} \quad (8.16)$$

and the “natural” variables are T and P , so

$$G = \hat{\mathcal{G}}(T, P) \stackrel{(8.15)}{=} \hat{\mathcal{H}}(T, P) - T \hat{\mathcal{S}}(T, P), \quad \text{with} \quad \frac{\partial \hat{\mathcal{G}}}{\partial T}(T, P) = -\hat{\mathcal{S}}(T, P), \quad \frac{\partial \hat{\mathcal{G}}}{\partial P}(T, P) = \hat{\mathcal{V}}(T, P). \quad (8.17)$$

Thermodynamic notation (reversible transformation): $G := H - TS$ with

$$dG = V dP - S dT, \quad \text{i.e.} \quad \frac{\partial G}{\partial T}|_P = -S, \quad \frac{\partial G}{\partial P}|_T = V. \quad (8.18)$$

Interpretation. « The free enthalpy is a criterion of spontaneity of a chemical reaction : $dG < 0$ for a spontaneous reaction , $dG = 0$ at equilibrium. »

(See <http://forums.futura-sciences.com/chimie/19331-enthalpie-libre.html>.)

(See http://biologie.univ-mrs.fr/upload/p290/Cours_thermo.pdf.)

Exercice 8.4 Prove: $\frac{\partial G}{\partial T} = -\frac{H}{T^2}$.

Answer. Let $z(T, P) := \frac{G(T, P)}{T}$, i.e. $z(T, P) = \frac{H(S(T, P), P)}{T} - S(T, P)$. Hence

$$\frac{\partial G}{\partial T}(T, P) := \frac{\partial z}{\partial T}(T, P) = -\frac{H(S(T, P), P)}{T^2} + \frac{1}{T} \frac{\partial H}{\partial S}(S(T, P), P) \frac{\partial S}{\partial T}(T, P) - \frac{\partial S}{\partial T}(T, P), \quad (8.19)$$

with $\frac{\partial H}{\partial S}(S(T, P), P) = T$, cf. (8.2). \blacksquare

9 Gibbs–Duhem equation

The internal energy being extensive, $\bar{U}(\lambda S, \lambda V) = \lambda \bar{U}(S, V)$, i.e. \bar{U} is homogeneous of degree 1. Thus the Euler relation gives, cf. (B.3),

$$\bar{U}(S, V) = S \frac{\partial \bar{U}}{\partial S}(S, V) + V \frac{\partial \bar{U}}{\partial V}(S, V). \quad (9.1)$$

Thus, $\delta W = -P dV$, a reversible transformation, and $\frac{\partial \bar{U}}{\partial S}(S, V) = \bar{T}(S, V)$ and $\frac{\partial \bar{U}}{\partial V}(S, V) = -\bar{P}(S, V)$ cf. (7.9), give

$$\bar{U}(S, V) = S \bar{T}(S, V) - V \bar{P}(S, V). \quad (9.2)$$

Thermodynamic notation: $U = ST - VP$. Thus, formally,

$$dU = T dS + S dT - P dV - V dP, \quad \text{with} \quad dU = T dS - P dV, \quad \text{thus} \quad S dT - V dP = 0, \quad (9.3)$$

which rigorously means

$$S d\bar{T}(S, V) - V d\bar{P}(S, V) = 0. \quad (9.4)$$

Thus $S(\frac{\partial \bar{T}}{\partial S}(S, V) dS + \frac{\partial \bar{T}}{\partial V}(S, V) dV) - V(\frac{\partial \bar{P}}{\partial S}(S, V) dS + \frac{\partial \bar{P}}{\partial V}(S, V) dV) = 0$, thus $S \frac{\partial \bar{T}}{\partial S}(S, V) - V \frac{\partial \bar{P}}{\partial S}(S, V) = 0$ and $S \frac{\partial \bar{T}}{\partial V}(S, V) - V \frac{\partial \bar{P}}{\partial V}(S, V) = 0$, that is, with thermodynamic notation (reversible transformation):

$$S \frac{\partial T}{\partial S}|_V - V \frac{\partial P}{\partial S}|_V = 0 \quad \text{and} \quad S \frac{\partial T}{\partial V}|_S - V \frac{\partial P}{\partial V}|_S = 0 \quad (\text{Gibbs–Duhem equations}). \quad (9.5)$$

Appendix

A Composite functions

Proposition A.1 If $\vec{X} \in C^1(\mathbb{R}^n; \mathbb{R}^m)$, $f \in C^1(\mathbb{R}^m; \mathbb{R})$ and $g = f \circ \vec{X} \in C^1(\mathbb{R}^n; \mathbb{R})$, i.e. $g(\vec{x}) = f(\vec{X}(\vec{x}))$, then

$$dg(\vec{x}) = df(\vec{X}(\vec{x})).d\vec{X}(\vec{x}), \quad (\text{A.1})$$

i.e., with Cartesian bases, for all $i = 1, \dots, n$, $\vec{X} = (X_1, \dots, X_m)$ and $\vec{x} = (x_1, \dots, x_n)$,

$$\frac{\partial g}{\partial x_i}(\vec{x}) = \sum_{j=1}^m \frac{\partial f}{\partial X_j}(\vec{X}(\vec{x})) \frac{\partial X_j}{\partial x_i}(\vec{x}), \quad (\text{A.2})$$

or $\partial_i g(\vec{x}) = \sum_{j=1}^m \partial_j f(\vec{X}(\vec{x})) \partial_i X_j(\vec{x})$ (with unambiguous notation independent of the variable names).

Proof. $m = n = 2$ for readability, so $g(x_1, x_2) = f(X_1(x_1, x_2), X_2(x_1, x_2))$. And

$$\begin{aligned} g(x_1+h, x_2) &= f(\vec{X}(x_1+h, x_2)) = f(X_1(x_1+h, x_2), X_2(x_1+h, x_2)) \\ &= f\left(X_1(x_1, x_2) + h \frac{\partial X_1}{\partial x_1}(x_1, x_2) + o(h), X_2(x_1, x_2) + h \frac{\partial X_2}{\partial x_1}(x_1, x_2) + o(h)\right) \\ &\stackrel{(2.2)}{=} f(\vec{X}(\vec{x})) + h df(\vec{X}(\vec{x})) \cdot \left(\frac{\partial X_1}{\partial x_1}(\vec{x}) + o(1), \frac{\partial X_2}{\partial x_1}(\vec{x}) + o(1)\right) + o(h) \\ &\stackrel{(2.3)}{=} g(\vec{x}) + h \frac{\partial f}{\partial X_1}(\vec{X}(\vec{x})) \left(\frac{\partial X_1}{\partial x_1}(\vec{x}) + o(1)\right) + h \frac{\partial f}{\partial X_2}(\vec{X}(\vec{x})) \left(\frac{\partial X_2}{\partial x_1}(\vec{x}) + o(1)\right) + o(h), \end{aligned}$$

thus $\frac{g(x_1+h, x_2) - g(x_1, x_2)}{h} \xrightarrow{h \rightarrow 0} \frac{\partial f}{\partial X_1}(\vec{X}(\vec{x})) \frac{\partial X_1}{\partial x_1}(\vec{x}) + \frac{\partial f}{\partial X_2}(\vec{X}(\vec{x})) \frac{\partial X_2}{\partial x_1}(\vec{x})$. \blacksquare

Exercise A.2 Let $f \in C^1(\mathbb{R}^2; \mathbb{R})$. Let $g(x, y) := f(\lambda x, \lambda y)$. Compute $\frac{\partial g}{\partial x}$ in terms of $\frac{\partial f}{\partial x}$ and $\frac{\partial f}{\partial y}$.

Answer. 1- $X(x, y) = \lambda x$ and $Y(x, y) = \lambda y$ give $\frac{\partial X}{\partial x}(x, y) = \lambda = \partial_1 X(x, y)$, $\frac{\partial Y}{\partial x}(x, y) = 0 = \partial_1 Y(x, y)$, ..., thus $\frac{\partial g}{\partial x}(x, y) = \frac{\partial f}{\partial X}(\lambda x, \lambda y) \lambda + 0 \stackrel{\text{noted}}{=} \frac{\partial f}{\partial(\lambda x)}(\lambda x, \lambda y) \lambda$, and $\frac{\partial g}{\partial y}(x, y) = 0 + \frac{\partial f}{\partial Y}(\lambda x, \lambda y) \lambda \stackrel{\text{noted}}{=} \frac{\partial f}{\partial(\lambda y)}(\lambda x, \lambda y) \lambda$. \blacksquare

Exercise A.3 Let $f \in C^1(\mathbb{R}^2; \mathbb{R})$ and $g(x) = \int_{t=0}^x f(x, t) dt$ (integral which depends on x). Compute g' .

Answer. Here $g(x) = F(\vec{X}(x))$ where $F(X, Y) = \int_{t=0}^Y f(X, t) dt$; And $\frac{\partial F}{\partial X}(X, Y) = \int_{t=0}^Y \frac{\partial f}{\partial X}(X, t) dt$ and $\frac{\partial F}{\partial Y}(X, Y) = f(X, Y)$, hence $g'(x) = \int_{t=0}^x \frac{\partial f}{\partial x}(x, t) dt + f(x, x)$. \blacksquare

B Homogeneous function of degree k , Euler theorem

Let $\mathbb{R}_+^n = \{\vec{x} = (x_1, \dots, x_n) \in \mathbb{R}^n : x_i \geq 0, \forall i = 1, \dots, n\}$.

Definition B.1 $f : \mathbb{R}_+^n \rightarrow \mathbb{R}$ is homogeneous of degree (or of order) $k \in \mathbb{R}^*$ iff, for all $\lambda > 0$ and all $\vec{x} \in \mathbb{R}_+^n$,

$$f(\lambda \vec{x}) = \lambda^k f(\vec{x}), \quad \text{i.e.} \quad f(\lambda x_1, \dots, \lambda x_n) = \lambda^k f(x_1, \dots, x_n). \quad (\text{B.1})$$

I.e., the function $\phi_{\vec{x}} : \lambda \in \mathbb{R}_+^* \rightarrow \phi_{\vec{x}}(\lambda) = f(\lambda \vec{x})$ satisfies $\phi_{\vec{x}}(\lambda) = \lambda^k \phi_{\vec{x}}(1)$ (degree k monomial).

Example B.2 $n = 2$. $p, q \in \mathbb{R}$, $f(x, y) = x^p y^q$ and $x, y > 0$: Thus $f(\lambda x, \lambda y) = \lambda^{p+q} f(x, y)$, so f is homogeneous of degree $p+q$. E.g., $f(x, y) = \sqrt{xy}$ and $f(x, y) = xy$ are homogeneous of degree 1 and 2.

$g, h : \mathbb{R} \rightarrow \mathbb{R}$ and $f : (x, y) \in \mathbb{R}^* \times \mathbb{R}^* \rightarrow f(x, y) = ax^k g(\frac{y}{x}) + by^k h(\frac{x}{y})$: f is homogeneous of degree k . \blacksquare

Theorem B.3 Euler. If $f \in C^1(\mathbb{R}_+^n; \mathbb{R})$ is homogeneous of degree $k \in \mathbb{R}^{n*}$, then

$$k \lambda^{k-1} f(\vec{x}) = \sum_{i=1}^n x_i \partial_i f(\lambda \vec{x}) \stackrel{\text{noted}}{=} \sum_{i=1}^n x_i \frac{\partial f}{\partial(\lambda x_i)}(\lambda \vec{x}). \quad (\text{B.2})$$

In particular $\lambda = 1$ gives

$$k f(\vec{x}) = \sum_{i=1}^n x_i \frac{\partial f}{\partial x_i}(\vec{x}). \quad (\text{B.3})$$

And $\partial_i f \stackrel{\text{noted}}{=} \frac{\partial f}{\partial x_i}$ is homogeneous of degree $k-1$: For all $\lambda > 0$, $\vec{x} \in \mathbb{R}_+^n$ and $i = 1, \dots, n$,

$$\partial_i f(\lambda \vec{x}) = \lambda^{k-1} \partial_i f(\vec{x}), \quad \text{written} \quad \frac{\partial f}{\partial(\lambda x_i)}(\lambda \vec{x}) = \lambda^{k-1} \frac{\partial f}{\partial x_i}(\vec{x}). \quad (\text{B.4})$$

Proof. Fix \vec{x} , and let $\phi(\lambda) := f(\lambda\vec{x}) = f(\lambda x_1, \dots, \lambda x_n)$. So $\phi(\lambda) = f(\vec{X}(\lambda)) = f(X_1(\lambda), \dots, X_n(\lambda))$ where $X_i(\lambda) = \lambda x_i$. Thus

$$\phi'(\lambda) = \sum_{i=1}^n \frac{\partial f}{\partial X_i}(\lambda\vec{x}) X_i'(\lambda) = \sum_{i=1}^n \frac{\partial f}{\partial X_i}(\lambda\vec{x}) x_i.$$

And $\phi(\lambda) = \lambda^k \phi(1)$, thus $\phi'(\lambda) = k\lambda^{k-1} \phi(1) = k\lambda^{k-1} f(\vec{x})$, thus $\sum_{i=1}^n x_i \frac{\partial f}{\partial X_i}(\lambda\vec{x}) = k\lambda^{k-1} f(\vec{x})$.

Then fix x_2, \dots, x_n . Let $h(x) = f(\lambda x, \lambda x_2, \dots, \lambda x_n)$, so $= \lambda^k f(x, x_2, \dots, x_n)$, thus

$$(h'(x) =) \lambda \frac{\partial f}{\partial X_1}(\lambda x, \lambda x_2, \dots, \lambda x_n) = \lambda^k \frac{\partial f}{\partial X_1}(x, x_2, \dots, x_n),$$

Then simplify by λ and take $x = x_1$. Idem with x_2, x_3, \dots ▀

C Cyclic equalities

C.1 With two linked variables: $\frac{\partial x}{\partial y} \frac{\partial y}{\partial x} = 1$

Hypothesis: 2 variables x, y are linked, i.e. we have an implicit equation

$$Z(x, y) = 0. \quad (\text{C.1})$$

Proposition C.1 If $Z \in C^1(\mathbb{R}^2; \mathbb{R})$ with $\frac{\partial Z}{\partial x}(x, y) \neq 0$ and $\frac{\partial Z}{\partial y}(x, y) \neq 0$, then $\exists f_1, f_2 \in C^2(\mathbb{R}; \mathbb{R})$ s.t.

$$f_1(f_2(x)) \cdot f_2'(x) = 1, \quad \text{written} \quad \frac{df_1}{dy}(y) \frac{df_2}{dx}(x) = 1, \quad \text{written} \quad \frac{dx}{dy} \frac{dy}{dx} = 1. \quad (\text{C.2})$$

Proof. Apply the implicit function theorem (since Z is C^1 with $\frac{\partial Z}{\partial x}(x, y) \neq 0$ and $\frac{\partial Z}{\partial y}(x, y) \neq 0$ for all x, y): The functions f_1 et f_2 exist, are C^1 , and $x = (f_1 \circ f_2)(x)$, thus $1 = f_1'(f_2(x)) f_2'(x)$. ▀

Example C.2 Perfect gas with $n = n_0$ and $V = V_0$ fixed : $Z(T, P) = PV_0 - n_0 RT = 0$. Thus $T = f_1(P) = \frac{V_0}{n_0 R} P$, and $P = f_2(T) = \frac{n_0 R}{V_0} T$. And $(f_1 \circ f_2)(T) = \frac{V_0}{n_0 R} (\frac{n_0 R}{V_0} T) = T$ as wished. And $\frac{\partial Z}{\partial T}(T, P) = n_0 R \neq 0$ and $\frac{\partial Z}{\partial P}(T, P) = V_0 \neq 0$. And $f_1'(P) = \frac{V_0}{n_0 R}$ and $f_2'(T) = \frac{n_0 R}{V_0}$ satisfy $f_1'(P) f_2'(T) = 1$, written $\frac{dT}{dP}(P) \cdot \frac{dP}{dT}(T) = 1$, or $\frac{dT}{dP} \cdot \frac{dP}{dT} = 1$. ▀

Generalization. $n \geq 2$ and n variables x, y, z_3, \dots, z_n with

$$Z(x, y, z_3, \dots, z_n) = 0 \stackrel{\text{noted}}{=} Z_{z_3, \dots, z_n}(x, y), \quad (\text{C.3})$$

where here z_3, \dots, z_n are considered to be parameters: We get

$$\frac{\partial f_1}{\partial y}(y, z_3, \dots, z_n) \frac{\partial f_2}{\partial x}(x, z_3, \dots, z_n) = 1 \quad \text{when} \quad y = f_2(x, z_3, \dots, z_n). \quad (\text{C.4})$$

Thermodynamic notation:

$$\frac{\partial x}{\partial y} \Big|_{z_3, \dots, z_n} \frac{\partial y}{\partial x} \Big|_{z_3, \dots, z_n} = 1. \quad (\text{C.5})$$

Example C.3 Perfect gas: $Z(T, P, V, n) = PV - nRT$. Thus $T = f_1(P, V, n) = \frac{V}{nR} P$, and $P = f_2(T, V, n) = \frac{nR}{V} T$. We check: $(f_1 \circ f_2)(T, V, n) = \frac{V}{nR} (\frac{nR}{V} T) = T$ and $\frac{\partial T}{\partial P} \Big|_{V, n} \frac{\partial P}{\partial T} \Big|_{V, n} = 1$. ▀

C.2 With three linked variables: $\frac{\partial x}{\partial y} \frac{\partial y}{\partial z} \frac{\partial z}{\partial x} = -1$

Three variables x, y, z are linked, i.e. we have an implicit equation

$$Z(x, y, z) = 0. \quad (\text{C.6})$$

Proposition C.4 Let $x_i = x$ or y or z . If Z is C^1 , and $\frac{\partial Z}{\partial x_i}(x, y, z) \neq 0$ for all x, y, z and i , then

$$\frac{\partial f_1}{\partial y}(y, z) \frac{\partial f_2}{\partial z}(z, x) \frac{\partial f_3}{\partial x}(x, y) = -1, \quad \text{written} \quad \frac{\partial x}{\partial y} \Big|_z \frac{\partial y}{\partial z} \Big|_x \frac{\partial z}{\partial x} \Big|_y = -1 \quad (\text{thermo notations}). \quad (\text{C.7})$$

(Circular permutation for the variables.)

Proof. $\left\{ \begin{array}{l} Z(f_1(y, z), y, z) = 0, \\ Z(x, f_2(z, x), z) = 0, \\ Z(x, y, f_3(x, y)) = 0. \end{array} \right\}$ gives $\left\{ \begin{array}{l} \frac{\partial Z}{\partial x} \frac{\partial f_1}{\partial y} + \frac{\partial Z}{\partial y} = 0, \\ \frac{\partial Z}{\partial y} \frac{\partial f_2}{\partial z} + \frac{\partial Z}{\partial z} = 0, \\ \frac{\partial Z}{\partial x} + \frac{\partial Z}{\partial z} \frac{\partial f_3}{\partial x} = 0, \end{array} \right\}$ where the notations have been abusively

lightened for readability. Multiply the first equation by $\frac{\partial f_2}{\partial z}$ and subtract the second equation:

$$\left\{ \begin{array}{l} \frac{\partial Z}{\partial x} \frac{\partial f_1}{\partial y} \frac{\partial f_2}{\partial z} - \frac{\partial Z}{\partial z} = 0, \\ \frac{\partial Z}{\partial x} + \frac{\partial Z}{\partial z} \frac{\partial f_3}{\partial x} = 0. \end{array} \right.$$

Multiply the first equation by $\frac{\partial f_3}{\partial x}$ and add the second equation: $\frac{\partial Z}{\partial x} \frac{\partial f_1}{\partial y} \frac{\partial f_2}{\partial z} \frac{\partial f_3}{\partial x} + \frac{\partial Z}{\partial x} = 0$, thus (C.7). ■

Generalization, n variables x, y, z, t_4, \dots, t_n ; Thermodynamic notation:

$$\frac{\partial x}{\partial y|_{z, u_4, \dots, u_n}} \frac{\partial y}{\partial z|_{x, u_4, \dots, u_n}} \frac{\partial z}{\partial x|_{y, u_4, \dots, u_n}} = -1. \quad (\text{C.8})$$