

Thermodynamics

– Understanding –

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Goal: 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

1.1 Usual notations

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 an imposed 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 $[\vec{v}] = \begin{pmatrix} v_1 \\ \vdots \\ v_n \end{pmatrix}$.

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 real 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 $(\lambda \cdot f)(x) := \lambda(f(x))$.

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

Definition 1.1 A linear form ℓ on E is function $\ell \in \mathcal{F}(E; \mathbb{R})$ which is linear, i.e. s.t. $\ell(\vec{v} + \lambda \vec{w}) = \ell(\vec{v}) + \lambda \ell(\vec{w})$ for all $\vec{v}, \vec{w} \in E$ and $\lambda \in \mathbb{R}$. And

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

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

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

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, with \mathbb{R} the field used to build the vector space $\mathcal{F}(E; \mathbb{R})$:

- The “dimension” (length, temperature, pressure, volume...) of a vector \vec{v} is denoted $\{\vec{v}\}$.
- If $\lambda \in \mathbb{R}$ then $\{\lambda\} := 1$, and λ is dimensionless.
- If $\lambda \in \mathbb{R}$ and $\vec{v}_2 = \lambda \vec{v}$, the “dimension calculus” gives $\{\vec{v}_2\} = \{\lambda \vec{v}\} = \{\lambda\} \{\vec{v}\} = 1 \{\vec{v}\} = \{\vec{v}\}$ (as expected: \vec{v}_2 and \vec{v} have the same dimension). E.g., if \vec{e}_1 is a basis vector modeling a wooden stick of length 1 foot, and if $\vec{v} = 3\vec{e}_1$, then $\{\vec{v}\} = \{\vec{e}_1\}$ and the length of \vec{v} is $\lambda = 3$ (dimensionless) relative to \vec{e}_1 .
- 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

$$\{\ell\} = \{\vec{v}\}^{-1}. \tag{1.2}$$

E.g., $\dim E = 1$, \vec{e}_1 is a basis vector modeling a wooden stick of length 1 foot, $\ell_1 \in E^*$ is the linear form “the measuring tool” defined by $\ell_1 \cdot \vec{e}_1 = 1$: if $\vec{v} = \lambda \vec{e}_1$ then $\{\vec{v}\} = \{\vec{e}_1\}$ (same dimension), $\{\lambda\} = 1$ (no dimension) with $\lambda = \ell_1 \cdot \vec{v}$, the length of \vec{v} being λ relative to (\vec{e}_1) , i.e. the length of \vec{v} is λ in foot.

Remark: (1.2) tells that the dimension of a linear form, called “a covariant vector”, is the inverse of the dimension of a vector called “a contravariant vector”.

• The dimension of a bilinear form $g : (\vec{v}, \vec{w}) \in E \times E \rightarrow g(\vec{u}, \vec{v}) = (\vec{u}, \vec{v})_g \in \mathbb{R}$ is given by $\{g(\vec{u}, \vec{v})\} = 1$ (dimension of a real); And $\{g(\vec{u}, \vec{v})\} = \{g\}\{\vec{u}\}\{\vec{v}\}$ (no dimension), thus

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

(And $g(\cdot, \cdot)$ is “twice covariant”).

1.3 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 $\pi_i(\vec{e}_j) = \delta_{ij}$, i.e. (linearity notation)

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

for all $i, j = 1, \dots, n$. I.e. $\pi_i(\vec{e}_i) = 1$, and $\pi_i(\vec{e}_j) = 0$ if $i \neq j$.

Interpretation: 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 If $\vec{X} = T\vec{e}_1 + P\vec{e}_2 \in \mathbb{R}^2$, where \vec{e}_1 models 1 Kelvin degree and \vec{e}_2 models 1 Pascal, then π_1 gives the temperature in Kelvin and π_2 gives pressure in Pascal: $\pi_1(\vec{X}) = T$ and $\pi_2(\vec{X}) = P$. ■

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

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

Thus, for all $\vec{v} = \sum_i v_i \vec{e}_i$,

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

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 $a_j = 0$, true 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 (E^* is a vector space) and $g(\vec{e}_j) = \sum_{i=1}^n \ell_i \pi_i(\vec{e}_j) = \sum_{i=1}^n \ell_i \delta_{ij} = \ell_j = \ell(\vec{e}_j)$, 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 $\ell \cdot \vec{v} = (\sum_j \ell_j \pi_j) \cdot (\sum_i v_i \vec{e}_i) = \sum_{ij} \ell_j v_i \pi_j(\vec{e}_i) = \sum_{ij} \ell_j v_i \delta_{ij} = \sum_j \ell_j v_j = [\ell] \cdot [\vec{v}]$. ■

1.4 Cartesian setting: Notations for the dual basis

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

$$\pi_1 \stackrel{\text{noted}}{=} dx, \quad \pi_2 \stackrel{\text{noted}}{=} dy, \dots, \quad \text{and } \ell = \ell_1 dx + \ell_2 dy + \dots \quad (1.8)$$

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

$$\pi_1 \stackrel{\text{noted}}{=} dT, \quad \pi_2 \stackrel{\text{noted}}{=} dP, \dots, \quad \text{and } \ell = \ell_1 dT + \ell_2 dP + \dots \quad (1.9)$$

2 Differential

2.1 Definition and partial derivatives

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

$$\phi(\vec{x}) = \underbrace{\phi(\vec{x}_0) + d\phi(\vec{x}_0) \cdot (\vec{x} - \vec{x}_0)}_{a_{\vec{x}_0}(\vec{x}) = \text{affine approx.}} + o(\|\vec{x} - \vec{x}_0\|). \quad (2.1)$$

(2.1) is the first order Taylor development of ϕ near \vec{x}_0 , and the affine function $a_{\vec{x}_0} : \vec{x} \rightarrow a_{\vec{x}_0}(\vec{x}) = \phi(\vec{x}_0) + d\phi(\vec{x}_0) \cdot (\vec{x} - \vec{x}_0)$ 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). I.e., 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 ; And the differential of ϕ is 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 . And $C^1(\Omega; \mathbb{R})$ is 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 $d\phi(\vec{x}_0) \cdot \vec{v}$ is the directional derivative of ϕ in the direction \vec{v} at \vec{x} .

In particular, with (\vec{e}_i) a basis in E and $\vec{v} = \vec{e}_i$, the i -th partial derivative of ϕ at \vec{x} is

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

This defines $\partial_i \phi = \text{noted } \frac{\partial \phi}{\partial x_i} : \left\{ \begin{array}{l} \Omega \rightarrow \mathbb{R} \\ \vec{x} \rightarrow d\phi(\vec{x}) \cdot \vec{e}_i \end{array} \right\}$ 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) and (2.4):

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

$$d\phi(\vec{x}) = \frac{\partial \phi}{\partial x_1}(\vec{x}) \pi_1 + \dots + \frac{\partial \phi}{\partial x_n}(\vec{x}) \pi_n, \quad \text{i.e.} \quad [d\phi(\vec{x})] = \left(\frac{\partial \phi}{\partial x_1}(\vec{x}) \quad \dots \quad \frac{\partial \phi}{\partial x_n}(\vec{x}) \right) \quad (2.5)$$

row matrix called the Jacobian matrix of ϕ at \vec{x} . With $\pi_i = \text{noted } dx_i$ (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 $\vec{v} = \sum_{i=1}^n v_i \vec{e}_i$.

And e.g. with $\vec{x} = (x, y, \dots)$ or $\vec{x} = (T, P, \dots)$ and (1.8) or (1.9), then

$$d\phi(x, y) = \frac{\partial \phi}{\partial x}(x, y) dx + \frac{\partial \phi}{\partial y}(x, y, \dots) dy, \quad d\phi(T, P) = \frac{\partial \phi}{\partial T}(T, P) dT + \frac{\partial \phi}{\partial P}(T, P, \dots) dP. \quad (2.7)$$

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

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

the last equation being the thermodynamical notations. ▀

3 Differential forms

3.1 Definition

Definition 3.1 Ω being an open (non empty) set in E , a differential form in Ω is function $\alpha \in \mathcal{F}(E; E^*)$. And $\Omega^1(\Omega)$ is the set of C^∞ differential forms in Ω .

So $\alpha(\vec{x}) \in E^*$ (is a linear form) and $\alpha(\vec{x}) \cdot \vec{v} \in \mathbb{R}$ (measured value along \vec{v}), for all $\vec{x} \in \Omega$ and $\vec{v} \in \mathbb{R}^n$.

Components. $(\pi_i) = {}^{noted}(dx_i)$ being the dual basis of a Cartesian basis (\vec{e}_i) in E ,

$$\alpha(\vec{x}) = \alpha_1(\vec{x}) dx_1 + \dots + \alpha_n(\vec{x}) dx_n, \quad \text{i.e.} \quad [\alpha(\vec{x})] = (\alpha_1(\vec{x}) \quad \dots \quad \alpha_n(\vec{x})) \quad (\text{row matrix}), \quad (3.1)$$

where $\alpha_i(\vec{x}) := \alpha(\vec{x}) \cdot \vec{e}_i$ (the i -th component of $\alpha(\vec{x})$).

3.2 Exact differential form

Definition 3.2 Let α be a differential form in Ω . If $\exists \phi \in C^1(\Omega; \mathbb{R})$ s.t. $\alpha = d\phi$ then α is said to be exact in Ω , and α is said to derive from the potential ϕ , or α is conservative, and ϕ is a primitive of α . Otherwise α is not exact.

So, with a Cartesian basis (\vec{e}_i) , if α is exact then $\alpha = d\phi$ gives

$$\alpha(\vec{x}) = \frac{\partial \phi}{\partial x_1}(\vec{x}) \pi_1 + \frac{\partial \phi}{\partial x_2}(\vec{x}) \pi_2 + \dots, \quad [\alpha] = \left(\frac{\partial \phi}{\partial x_1} \quad \frac{\partial \phi}{\partial x_2} \quad \dots \right). \quad (3.2)$$

Example 3.3 (Non exact differential form.) $n = 2$; Consider the differential form (“dissipative energy”)

$$\alpha(x, y) = -y dx + x dy, \quad \text{i.e.} \quad [\alpha(x, y)] = (-y \quad x). \quad (3.3)$$

This differential form is **not** exact: If α was exact then $\exists \phi \in C^1$ 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 $\phi \in C^1$, thus $\frac{\partial \phi}{\partial y}(\vec{x}) = -x + g'(y)$; Together with $\frac{\partial \phi}{\partial y}(\vec{x}) = x$, thus $g'(y) = 2x$ for all $\vec{x} = (x, y) \in \Omega$ (not empty); Absurd: $\vec{x}_1 = (x_1, y)$ and $\vec{x}_2 = (x_2, y)$ with $x_1 \neq x_2$ give $g'(y) \neq g'(y)$. Thus α is not exact. (Remark: If you looked for a $\phi \in C^2$ then Schwartz’s theorem gives $\frac{\partial \frac{\partial \phi}{\partial x}}{\partial y}(\vec{x}) = \frac{\partial \frac{\partial \phi}{\partial y}}{\partial x}(\vec{x})$, thus $-1 = +1$: Absurd.) ■

Remark 3.4 The first principle tells : A “material” has a internal energy U which is a potential, which means: The density of internal energy is an exact differential form dU . Moreover $dU = \alpha + \beta$ is the sum of two differential forms α and β , non exact in general, called the elementary heat $\alpha = {}^{noted} \delta Q$ and the elementary work $\beta = {}^{noted} \delta W$, so $dU = \delta Q + \delta W$.

(Definition of the differential form “the heat”: If $\beta = \delta W$ is the mechanical work, then $\alpha = dU - \beta$ is called the heat.) ■

3.3 Curves, paths, trajectories

Definition 3.5 Let $t_0, t_f \in \mathbb{R}$, $t_0 < t_f$, and let Ω be an open subset in E .

A (parametric) curve or path in Ω is a function $\vec{r} \in C^1([t_0, t_f]; \Omega)$.

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

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

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

Definition 3.6 The tangent vector along \vec{r} at $\vec{x} = \vec{r}(t)$ is $\vec{v}(\vec{x}) := \vec{r}'(t) \in E$. I.e. $\vec{v}(\vec{r}(t)) = \lim_{h \rightarrow 0} \frac{\vec{r}(t+h) - \vec{r}(t)}{h}$ 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 (and its norm is the speed).

Notations: A Cartesian basis (\vec{e}_i) being chosen in E , if $\vec{x} = \vec{r}(t) = \sum_{i=1}^n r_i(t) \vec{e}_i$ then $\vec{v}(\vec{x}) = \vec{r}'(t) = \sum_{i=1}^n r_i'(t) \vec{e}_i = \sum_{i=1}^n v_i(\vec{x}) \vec{e}_i$, i.e. $[\vec{r}(t)] = \begin{pmatrix} r_1(t) \\ \vdots \\ r_n(t) \end{pmatrix}$, $[\vec{r}'(t)] = \begin{pmatrix} r_1'(t) \\ \vdots \\ r_n'(t) \end{pmatrix} = \begin{pmatrix} v_1(\vec{x}) \\ \vdots \\ v_n(\vec{x}) \end{pmatrix} = [\vec{v}(\vec{x})]$.

Example 3.7 \mathbb{R}^2 , (\vec{e}_i) Euclidean basis, $\vec{r}: [0, 2\pi] \rightarrow \mathbb{R}^2$ given by $[\vec{r}(t)] = \begin{pmatrix} x = r_1(t) = a + R \cos t \\ y = r_2(t) = b + R \sin t \end{pmatrix}$: $\text{Im} \vec{r}$ = radius R circle centered at (a, b) , and $[\vec{v}(\vec{x})] = [\vec{r}'(t)] = \begin{pmatrix} -R \sin t \\ R \cos t \end{pmatrix}$ = tangent vector at $\vec{x} = \vec{r}(t)$. ■

3.4 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 3.8 If $\alpha: \Omega \rightarrow E^*$ is a C^0 differential form, then its integral along \vec{r} is the real

$$\int_{\vec{r}} \alpha := \int_{t=t_0}^{t_f} \alpha(\vec{r}(t)) \cdot \vec{r}'(t) dt \stackrel{\text{noted}}{=} \int \alpha \cdot d\vec{r}. \quad (3.4)$$

Example 3.9 $[\alpha(x, y)] = (-y \ x)$ (example 3.3), $[\vec{r}(t)] = \begin{pmatrix} x = R \cos t \\ y = R \sin t \end{pmatrix}$, so $[\vec{r}'(t)] = \begin{pmatrix} -R \sin t \\ R \cos t \end{pmatrix}$, with $t \in [0, 2\pi]$. Thus (energy dissipation by friction)

$$\int_{\vec{r}} \alpha = \int_{t=0}^{2\pi} \alpha(\vec{r}(t)) \cdot \vec{r}'(t) dt = \int_{t=0}^{2\pi} R^2 dt = 2\pi R^2 \quad (3.5)$$

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

Proposition 3.10 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} :

$$\int_{\vec{r}} \alpha = \int_{\vec{r}} d\phi = \phi(\vec{r}(t_f)) - \phi(\vec{r}(t_0)) \quad (3.6)$$

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

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

thus

$$\int_{\vec{r}} d\phi \stackrel{(3.4)}{=} \int_{t_0}^{t_f} d\phi(\vec{r}(t)) \cdot \vec{r}'(t) dt = \int_{t_0}^{t_f} (\phi \circ \vec{r})'(t) dt = [(\phi \circ \vec{r})(t)]_{t_0}^{t_f} = \phi(\vec{r}(t_f)) - \phi(\vec{r}(t_0)).$$

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

Remark 3.11 Continuation of remark 3.4: $dU = \delta Q + \delta W$ with $\vec{x} = \vec{r}(t)$.

- $dU(\vec{x})$, $\delta Q(\vec{x})$ and $\delta W(\vec{x})$ are meaningful: They are differential forms at a point.
- $U(\vec{x})$ is meaningful: It is the potential at $\vec{x} = \vec{r}(t)$: With \vec{r} restricted to $[t_0, t]$, $U(\vec{x}) = U(\vec{x}_0) + \int_{\vec{r}} dU$.
- But $Q(\vec{x})$ et $W(\vec{x})$ are meaningless: Only $Q(\vec{r}) := \int_{\vec{r}} \delta Q = \int_{\tau=t_0}^t \delta Q(\vec{r}(\tau)) \cdot \vec{r}'(\tau) d\tau$ and $W(\vec{r}) := \int_{\vec{r}} \delta W = \int_{\tau=t_0}^t \delta W(\vec{r}(\tau)) \cdot \vec{r}'(\tau) d\tau$ are meaningful (quantities which depend on a trajectory). E.g. $\delta W = \alpha$ in (3.5) gives $\oint_{\vec{r}} \delta W \neq 0$, so δW is not an exact differential form, and $W(\vec{x}) = W(\vec{r}(t))$ is a nonsense.
- Vocabulary: U is an energy (at points), Q and W are “quantities of energy” (depend on a path). ■

4 Issue: Impossible gradient vector

4.1 Linear form and scalar dot product: Riesz representation vector

$(E, (\cdot, \cdot)_g)$ is a Hilbert space (always true if $\dim E < \infty$), i.e. E is a vector space, $(\cdot, \cdot)_g$ and $\|\cdot\|_g = \sqrt{(\cdot, \cdot)_g} \stackrel{\text{noted}}{=} \vec{v} \cdot \vec{w}$ are a scalar dot product and its associated norm in E , and E is complete with respect to $\|\cdot\|_g$. (A scalar dot product is a bilinear form $E \times E \rightarrow \mathbb{R}$ which is symmetric definite positive.)

Theorem 4.1 (Riesz representation theorem) If $\ell \in E^*$ is 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. $\text{Ker} \ell = \{\vec{v} \in E : \ell \cdot \vec{v} = 0\} = \ell^{-1}(\{\vec{0}\})$ is a closed hyperplane since ℓ is continuous. Let $\text{Ker} \ell^{\perp_g}$ be the $(\cdot, \cdot)_g$ -orthogonal space: $\text{Ker} \ell^{\perp_g} = \{\vec{w} \in E : \forall \vec{v}_0 \in \text{Ker} \ell, (\vec{w}, \vec{v}_0)_g = 0\}$; An orthogonal is always closed, hence $E = \text{Ker} \ell \oplus \text{Ker} \ell^{\perp_g}$. Suppose $\ell \neq 0$ (if $\ell = 0$ then $\vec{\ell}_g = \vec{0}$), thus $\dim \text{Ker} \ell^{\perp_g} = 1$ since $\text{Im} \ell = \mathbb{R}$. Choose a $\vec{w} \notin \text{Ker} \ell$, call \vec{w}_0 its $(\cdot, \cdot)_g$ -orthogonal projection on $\text{Ker} \ell$ (exists since $\text{Ker} \ell$ is closed). Let $\vec{n} := \frac{\vec{w} - \vec{w}_0}{\|\vec{w} - \vec{w}_0\|_g}$, so $\vec{n} \in \text{Ker} \ell^{\perp_g}$ and is $(\cdot, \cdot)_g$ -unitary. Thus if $\vec{v} \in E$ then $\vec{v} = \vec{v}_0 + \lambda \vec{n} \in \text{Ker} \ell \oplus \text{Ker} \ell^{\perp_g}$, thus $(\vec{v}, \vec{n})_g = 0 + \lambda$ and $\ell(\vec{v}) = 0 + \lambda \ell(\vec{n})$, thus $\ell(\vec{v}) = (\vec{v}, \vec{n})_g \ell(\vec{n}) = (\vec{v}, (\ell \cdot \vec{n})_g \vec{n})_g$. Thus $\vec{\ell}_g = (\ell \cdot \vec{n})_g \vec{n}$ satisfies (4.1). And uniqueness is trivial. 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 $\ell \neq 0$). \blacksquare

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

Remark 4.2 let α be a differential form. The Riesz representation theorem tells that $\alpha(\vec{x}) \in E^*$ can be represented its $(\cdot, \cdot)_g$ -Riesz representation vector $\vec{\alpha}_g(\vec{x}) =^{noted} \vec{f}(\vec{x})$ called a “force vector” ($(\cdot, \cdot)_g$ -dependent); Thus the work done by α along a path \vec{r} is

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

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

4.2 Definition of a gradient

Let E be finite dimensional, $f \in C^1(E; \mathbb{R})$, and $\vec{x} \in E$, so $df(\vec{x}) \in E^*$ (linear and continuous).

Definition 4.3 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 $\overrightarrow{\nabla_g f}(\vec{x})$ (depends on $(\cdot, \cdot)_g$). So, cf. (4.1),

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

If a $(\cdot, \cdot)_g$ is imposed and $(\vec{v}, \vec{w})_g =^{noted} \vec{v} \cdot \vec{w}$, then $\overrightarrow{\nabla_g f} =^{noted} \overrightarrow{\nabla f}$, thus $df(\vec{x}) \cdot \vec{v} = \overrightarrow{\nabla f}(\vec{x}) \cdot \vec{v}$. (Recall : $df(\vec{x})$ is covariant while $\overrightarrow{\nabla f}(\vec{x})$ is contravariant).

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

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

Issue: There is no physically meaningful scalar dot 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 : We must be content with dU .

5 Thermodynamic: vocabulary

5.1 Thermodynamic variables and functions

Let $[t_0, t_f] \subset \mathbb{R}$ be a time interval, $t_0 < t_f$, and \mathcal{O} be a non empty open set in the geometric space \mathbb{R}^3 .

Definition 5.1 A thermodynamic function is a function $X_i : \left\{ \begin{array}{l} [t_0, t_f] \times \mathcal{O} \rightarrow \mathbb{R} \\ (t, \vec{x}) \rightarrow X_i(t, \vec{x}) \end{array} \right\}$.

And $\vec{X} = (X_1, \dots, X_n) : [t_0, t_f] \times \mathcal{O} \rightarrow \mathbb{R}^n$ is the associated thermodynamic vector.

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 $X_i(t, \vec{x})$ is its value at t at \vec{x} .

E.g. $n=2$ and $\vec{X} = (T, P) : [t_0, t_f] \times \mathcal{O} \rightarrow \mathbb{R}^2$, where $\vec{X}(t, \vec{x}) = (T(t, \vec{x}), P(t, \vec{x}))$.

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

Definition 5.3 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 5.4 A system is in equilibrium iff the thermodynamic functions X_i are uniform in space, i.e., for all $t \in [t_0, t_f]$ and $i \in [1, n]_{\mathbb{N}}$,

$$\forall \vec{x}, \vec{y} \in \mathcal{O}, \quad X_i(t, \vec{x}) = X_i(t, \vec{y}), \quad \text{and then} \quad X_i(t, \vec{x}) \stackrel{\text{noted}}{=} X_i(t) \quad \text{and} \quad \vec{X}(t, \vec{x}) \stackrel{\text{noted}}{=} \vec{X}(t). \quad (5.1)$$

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

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

5.3 State function (“grandeur d’état”)

Definition 5.5 A state function (“grandeur d’état” in French) is a function

$$\phi : \begin{cases} \mathbb{R}^n & \rightarrow \mathbb{R}, \\ \vec{X} & \rightarrow \phi(\vec{X}), \end{cases} \quad (5.2)$$

where here \mathbb{R}^n is the name for the space of the state variables.

E.g. the “internal energy” $\phi = \mathcal{U} : (T, P) \rightarrow U = \mathcal{U}(T, P)$ (here $n=2$, $\vec{X} = (T, P)$, and Φ is defined on its definition domain $\subset \mathbb{R}^2$).

Definition 5.6 A state function is also the name given to a functional (= a function of functions)

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

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

The state functions ϕ will be supposed C^1 , hence

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

E.g.,

$$d\mathcal{U}(T, P) = \frac{\partial \mathcal{U}}{\partial T}(T, P) dT + \frac{\partial \mathcal{U}}{\partial P}(T, P) dP, \quad \text{written} \quad dU = \frac{\partial U}{\partial T|_P} dT + \frac{\partial U}{\partial P|_T} dP \quad (5.5)$$

(shorten thermo notation which in particular tells that the chosen variables are T and P).

E.g., $d\mathcal{U}(T, P, V) = \frac{\partial \mathcal{U}}{\partial T}(T, P, V) dT + \frac{\partial \mathcal{U}}{\partial P}(T, P, V) dP + \frac{\partial \mathcal{U}}{\partial V}(T, P, V) dV$, and shorten thermo 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 5.7 A state equation (or state law) is an implicit relation between the state variables:

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

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

Example 5.8 Perfect gas: $Z(T, P, V, n) = PV - nRT$ gives the state equation (state law) $PV - nRT = 0$, or $PV = nRT$, 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). \blacksquare

5.5 Extensive and intensive quantities

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

Definition 5.9 1. If $\psi(b_1) + \psi(b_2) = \psi(b_1 \cup b_2)$ for all $b_1, b_2 \in \mathcal{B}$, then ψ is said to be extensive (e.g., volume, number of particles, energy, entropy).

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

Remark 5.10 Extensivity and intensivity are also defined by: If B is cut in any two equal parts b_1 and b_2 then 1'- ψ is extensive iff $\psi(b_1) + \psi(b_2) = \psi(B)$, and 2'- ψ is intensive iff $\psi(b_1) = \psi(b_2) = \psi(B)$. ■

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

So, for a given material, with $\vec{X} = (T, P, V, \dots)$, and with QS the subset in $C^1([t_0, t_f]; \mathbb{R}^n)$ of quasi-static transformation $\vec{X} : t \in [t_0, t_f] \rightarrow \vec{X}(t) \in \mathbb{R}^n$, any material has an energy

$$U = \mathcal{U}(X) := \mathcal{U} \circ \vec{X}, \quad (6.1)$$

with $\mathcal{U} \in C^1(QS; \mathbb{R})$ the internal energy function, and with $\mathcal{U}(\vec{X})(t) := \mathcal{U}(\vec{X}(t))$ for all $\vec{X} \in QS$.

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:

$$\Delta U = Q + W. \quad (6.2)$$

So along any thermodynamical transformation $\vec{r} : t \in [t_0, t_f] \rightarrow \vec{r}(t) \in \mathbb{R}^n$, the heat received is defined to be $Q := \Delta U - W$, which means $Q(\vec{r}) = U(\vec{r}(t_f)) - U(\vec{r}(t_0)) - W(\vec{r})$.

2- And the heat and work, received along a thermodynamical transformation, are integrals of differential forms δQ and δW (non exact in general). So, for any quasi-static transformation $\vec{r} : [t_0, t_f] \rightarrow \mathbb{R}^n$,

$$dU = \delta Q + \delta W, \quad (6.3)$$

where

$$\begin{aligned} \bullet \Delta U &:= \mathcal{U}(\vec{r}(t_f)) - \mathcal{U}(\vec{r}(t_0)) \quad (= \Delta U(\vec{r}) = \int_{\vec{r}} dU = \int_{t_0}^{t_f} dU(\vec{r}(t)) \cdot \vec{r}'(t) dt), \\ \bullet Q &:= Q(\vec{r}) = \int_{\vec{r}} \delta Q \quad (= \int_{t_0}^{t_f} \delta Q(\vec{r}(t)) \cdot \vec{r}'(t) dt), \\ \bullet W &:= W(\vec{r}) = \int_{\vec{r}} \delta W \quad (= \int_{t_0}^{t_f} \delta W(\vec{r}(t)) \cdot \vec{r}'(t) dt). \end{aligned} \quad (6.4)$$

Remark 6.1 “Heat” and “work” are immaterial quantities (no “exchange of matter”); They are modeled by differential forms δQ and δW where $\delta Q(\vec{X})$ and $\delta W(\vec{X})$ are defined only after a trajectory \vec{r} has been considered and for $\vec{X} = \vec{r}(t)$. In particular, heat and work don’t exist if there is no transformation. So heat and work are not a characteristic of a body: They only exists temporarily. And $Q(\vec{r}) = \int_{\vec{r}} \delta Q = \int_{t_0}^{t_f} \delta Q(\vec{r}(t)) \cdot \vec{r}'(t) dt$ and $W(\vec{r}) = \int_{\vec{r}} \delta W = \int_{t_0}^{t_f} \delta W(\vec{r}(t)) \cdot \vec{r}'(t) dt$.

(And heat can only be exchanged spontaneously from a hot body to a cold body, irreversibility which 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 $\vec{X} = (T, P, V)$, $d\mathcal{U}(\vec{X}) = d\mathcal{U}(T, P, V)$, $\delta Q(\vec{X}) = \delta Q(T, P, V)$, $\delta W(\vec{X}) = \delta W(T, P, V)$.
- Isochoric transformation (e.g. bicycle pump, static piston, and we heat), i.e., at all time,

$$V = V_0 \quad (6.5)$$

and the remaining thermodynamical variables are T, P .

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

$$P = \tilde{\mathcal{P}}_{V_0}(T). \quad (6.6)$$

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

$$\tilde{\gamma}_{V_0} : \left\{ \begin{array}{l} [T_1, T_2] \rightarrow \mathbb{R}^3 \\ T \rightarrow \vec{X} = \tilde{\gamma}_{V_0}(T) = (T, \tilde{\mathcal{P}}_{V_0}(T), V_0) \end{array} \right\}, \quad \text{i.e.} \quad [\tilde{\gamma}_{V_0}(T)] = \begin{pmatrix} T \\ \tilde{\mathcal{P}}_{V_0}(T) \\ V_0 \end{pmatrix}. \quad (6.7)$$

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

$$\delta Q = d\mathcal{U} \quad \text{along } \tilde{\gamma}_{V_0}, \quad (6.8)$$

i.e. $\delta Q(\vec{X}) = d\mathcal{U}(\vec{X})$ at any $\vec{X} = \tilde{\gamma}_{V_0}(t)$: The elementary heat δQ is exact in $\text{Im}(\tilde{\gamma}_{V_0})$.

Definition 6.2 The thermal capacity per mole along $\tilde{\gamma}_{V_0}$ (so at constant volume V_0) is

$$C_{V_0} := \frac{1}{n} \lim_{\Delta T \rightarrow 0} \frac{\Delta Q}{\Delta T}, \quad \text{so} \quad nC_{V_0} := \frac{1}{n} \lim_{\Delta T \rightarrow 0} \frac{\Delta U}{\Delta T}. \quad (6.9)$$

So:

$$nC_{V_0}(\tilde{\gamma}_{V_0}(T)) = \lim_{h \rightarrow 0} \frac{U(\tilde{\gamma}_{V_0}(T+h)) - U(\tilde{\gamma}_{V_0}(T))}{h} = \frac{d(\mathcal{U} \circ \tilde{\gamma}_{V_0})}{dT}(T) = d\mathcal{U}(\tilde{\gamma}_{V_0}(T)) \cdot \tilde{\gamma}_{V_0}'(T). \quad (6.10)$$

And $\mathcal{U}(\tilde{\gamma}_{V_0}(T)) \cdot \tilde{\gamma}_{V_0}'(T) = [d\mathcal{U}(\tilde{\gamma}_{V_0}(T))] \cdot [\tilde{\gamma}_{V_0}'(T)]$, here with $[d\mathcal{U}] = \left(\frac{\partial \mathcal{U}}{\partial T} \quad \frac{\partial \mathcal{U}}{\partial P} \quad \frac{\partial \mathcal{U}}{\partial V} \right)$ and $[\tilde{\gamma}_{V_0}'(T)] =$ ^(6.7)
 $\begin{pmatrix} 1 \\ \tilde{\mathcal{P}}_{V_0}'(T) \\ 0 \end{pmatrix}$, thus

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

Thermo notations:

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

And $\delta Q = dU = nC_V dT$ along $\tilde{\gamma}_{V_0}$ gives $\int_{\tilde{\gamma}_{V_0}} \delta Q = \int_{\tilde{\gamma}_{V_0}} dU$, thus $Q(\tilde{\gamma}_{V_0}) = \int_{T_1}^{T_2} nC_{V_0}(\tilde{\gamma}_{V_0}(T)) dT$.

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

$$P = P_0, \quad (6.13)$$

and the remaining thermodynamical variables are T, V .

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

$$V = \widehat{V}_{P_0}(T). \quad (6.14)$$

Thus the only independent variable is T and the thermodynamic transformation is of the type

$$\vec{\gamma}_{P_0} : \left\{ \begin{array}{l} [T_1, T_2] \rightarrow \mathbb{R}^3 \\ T \rightarrow \vec{X} = \vec{\gamma}_{P_0}(T) = (T, P_0, \widehat{V}_{P_0}(T)) \end{array} \right\}, \quad \text{i.e.} \quad [\vec{\gamma}_{P_0}(T)] = \begin{pmatrix} T \\ P_0 \\ \widehat{V}_{P_0}(T) \end{pmatrix}. \quad (6.15)$$

- The only elementary work considered is $\delta W = -P dV$. Thus $dU = \delta Q - P dV$, thus, along $\vec{\gamma}_{P_0}$,

$$\delta Q(\vec{\gamma}_{P_0}(T)) = dU(\vec{\gamma}_{P_0}(T)) + P_0 d\widehat{V}_{P_0}(T), \quad (6.16)$$

and the elementary heat δQ is exact in $\text{Im}(\vec{\gamma}_{P_0})$.

Definition 6.3 The thermal capacity per mole along $\vec{\gamma}_{P_0}$ (so at constant pressure P_0) is

$$C_{P_0} := \frac{1}{n} \lim_{\Delta T \rightarrow 0} \frac{\Delta Q}{\Delta T}, \quad \text{i.e.} \quad C_{P_0} := \frac{1}{n} \lim_{\Delta T \rightarrow 0} \frac{\Delta U + P_0 \Delta V}{\Delta T}. \quad (6.17)$$

So

$$\begin{aligned} nC_{P_0}(\vec{\gamma}_{P_0}(T)) &= \lim_{h \rightarrow 0} \frac{\mathcal{U}(\vec{\gamma}_{P_0}(T+h)) - \mathcal{U}(\vec{\gamma}_{P_0}(T)) + P_0 \widehat{V}_{P_0}(T+h) - P_0 \widehat{V}_{P_0}(T)}{h} \\ &= \frac{d(\mathcal{U} \circ \vec{\gamma}_{P_0})}{dT}(T) + P_0 \widehat{V}_{P_0}'(T) = d\mathcal{U}(\vec{\gamma}_{P_0}(T)) \cdot \vec{\gamma}_{P_0}'(T) + P_0 \widehat{V}_{P_0}'(T). \end{aligned} \quad (6.18)$$

With $[d\mathcal{U}] = \left(\frac{\partial \mathcal{U}}{\partial T} \quad \frac{\partial \mathcal{U}}{\partial P} \quad \frac{\partial \mathcal{U}}{\partial V} \right)$ and $\vec{\gamma}_{P_0}'(T) \stackrel{(6.15)}{=} \begin{pmatrix} 1 \\ 0 \\ \widehat{V}_{P_0}'(T) \end{pmatrix}$ we get, at $\vec{X} = \vec{\gamma}_{P_0}(t)$ (along $\vec{\gamma}_{P_0}$),

$$nC_{P_0}(\vec{X}) = \frac{\partial \mathcal{U}}{\partial T}(\vec{X}) + 0 + \frac{\partial \mathcal{U}}{\partial V}(\vec{X}) \widehat{V}_{P_0}'(T) + P_0 \widehat{V}_{P_0}'(T). \quad (6.19)$$

Thermodynamic notations: along $\vec{\gamma}_P$,

$$nC_P dT = dU + P dV, \quad \text{and} \quad nC_P = \frac{\partial \mathcal{U}}{\partial T}|_{P,V} + \frac{\partial \mathcal{U}}{\partial V}|_{T,P} \frac{\partial V}{\partial T}|_P + P \frac{\partial V}{\partial T}|_P. \quad (6.20)$$

And $\delta Q = dU + P dV = nC_P dT$ along $\vec{\gamma}_{P_0}$, thus $Q(\vec{\gamma}_{P_0}) = \int_{T_1}^{T_2} nC_{P_0}(\vec{\gamma}_{P_0}(T)) dT$.

6.2.3 Enthalpy, and constant pressure transformation: C_P again

The number n of moles is constant (closed system), and the thermodynamical variables are T, P, V .

Definition 6.4 The enthalpy is $H := U + PV$, meaning

$$\mathcal{H}(T, P, V) = \mathcal{U}(T, P, V) + PV \quad \text{at} \quad \vec{X} = (T, P, V). \quad (6.21)$$

where $\mathcal{H} : \mathbb{R}^3 \rightarrow \mathbb{R}$ is the enthalpy function.

Definition 6.5 Suppose that the independent thermodynamical variables are T and P : This defines

$$\widehat{\mathcal{H}}(T, P) := \mathcal{H}(T, P, V(T, P)) \quad (= H = \mathcal{U}(T, P, \widehat{V}(T, P)) + P \widehat{V}(T, P)), \quad (6.22)$$

where $\widehat{\mathcal{H}} : \widehat{X} = (T, P) \in \mathbb{R}^2 \rightarrow \widehat{\mathcal{H}}(\widehat{X}) \in \mathbb{R}$ is also called an enthalpy function.

Thus $\frac{\partial \widehat{H}}{\partial T}(T, P) = \frac{\partial \mathcal{U}}{\partial T}(\vec{X}) + 0 + \frac{\partial \mathcal{U}}{\partial V}(\vec{X}) \frac{\partial \widehat{V}}{\partial T}(T, P) + P \frac{\partial \widehat{V}}{\partial T}(T, P)$. Thermo notations:

$$\frac{\partial H}{\partial T}|_P = \frac{\partial U}{\partial T}|_{P,V} + \frac{\partial U}{\partial V}|_{T,P} \frac{\partial V}{\partial T}|_P + P \frac{\partial V}{\partial T}|_P. \quad (6.23)$$

Then consider a transformation at constant pressure P_0 and let $\widehat{\mathcal{H}}_{P_0}(T) := \widehat{H}(T, P_0)$: The only variable left is T . thus with $\widehat{V}_{P_0}'(T) := \widehat{V}(T, P_0)$ we get at $\vec{X} = \vec{\gamma}_{P_0}(T) = (T, P_0, \widehat{V}_{P_0}'(T))$:

$$nC_{P_0}(\vec{X}) \stackrel{(6.19)}{=} \frac{d\widehat{\mathcal{H}}_{P_0}}{dT}(T), \quad \text{written} \quad nC_P = \frac{\partial H}{\partial T}|_P. \quad (6.24)$$

So: By definition of the enthalpy, C_{P_0} is the rate of variation of H along $\vec{\gamma}_{P_0}$ at $\vec{X} = \vec{\gamma}_{P_0}(T)$.

6.2.4 C_V vs C_P for a perfect gas, and the adiabatic index $\gamma = \frac{C_P}{C_V}$

Joule experiment: perfect gas approximated by “air at very low pressure” and $\vec{X} = (T, P, V)$.

First result: $U = \mathcal{U}(\vec{X})$ is independent of P and V , so $\frac{\partial \mathcal{U}}{\partial P} = \frac{\partial \mathcal{U}}{\partial V} = 0$, and $\mathcal{U}(\vec{X}) \stackrel{\text{noted}}{=} U(T)$. Thus

$$nC_V(\vec{X}) \stackrel{(6.11)}{=} \frac{dU}{dT}(T), \quad \text{and} \quad nC_P(\vec{X}) \stackrel{(6.19)}{=} \frac{dU}{dT}(T) + P \frac{\partial \widehat{V}}{\partial T}(T, P), \quad (6.25)$$

at $\vec{X} = (T, P, V)$ in a trajectory “at constant volume” and in a trajectory “at constant pressure”. And $PV = nRT$, thus $V = \widehat{V}(T, P) = \frac{nRT}{P}$ and $\frac{\partial \widehat{V}}{\partial T}(T, P) = \frac{nR}{P}$, thus

$$nC_P(\vec{X}) = nC_V(\vec{X}) + nR. \quad (6.26)$$

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

$$C_P = C_V + R. \quad (6.27)$$

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 6.6 The adiabatic index (ratio of molar heat capacities) is

$$\gamma := \frac{C_P}{C_V}, \quad \text{so} \quad \gamma = 1 + \frac{R}{C_V} \quad (> 1). \quad (6.28)$$

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

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

Definition 6.7 A (quasi-static) transformation is adiabatic iff $\delta Q = 0$ (no heat exchange, e.g. with “perfectly” insulated walls).

So here δW is an exact differential form ($= dU$). And the case treated is $\delta W = -P dV$.

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

Hypothesis: closed system, variables T, P, V , and T depends on P and V .

For perfect gases: $T = \widetilde{\mathcal{T}}(P, V) = \frac{PV}{nR}$ gives $d\widetilde{\mathcal{T}}(P, V) = \frac{1}{nR}V dP + \frac{1}{nR}P dV$, thus (thermodynamic notations)

$$dU \stackrel{(6.25)}{=} nC_V dT = nC_V \left(\frac{1}{nR}V dP + \frac{1}{nR}P dV \right) \quad (\text{perfect gas}). \quad (6.29)$$

Here with $dU = \delta Q + \delta W = 0 - P dV$, thus $\frac{C_V}{R}(V dP + P dV) = -P dV$, hence $(1 + \frac{R}{C_V})P dV + V dP = 0$. Thus, with $\gamma \stackrel{(6.28)}{=} 1 + \frac{R}{C_V}$,

$$\gamma \frac{dV}{V} + \frac{dP}{P} = 0, \quad \text{along an adiabatic path for a perfect gas.} \quad (6.30)$$

Hence

$$PV^\gamma = c = \text{constant, along an adiabatic path for a perfect gas.} \quad (6.31)$$

Exercice 6.8 Give rigorous steps to get (6.31).

Answer. Consider a trajectory $\vec{r} : t \in \rightarrow [\vec{r}(t)] = \begin{pmatrix} T(t) \\ P(t) \\ V(t) \end{pmatrix} \in \mathbb{R}^3$ s.t. $\delta Q(\vec{r}(t)) = 0$ for all t (adiabatic). With

$T \stackrel{\text{perfect}}{\text{gas}} \frac{PV}{nR}$ 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 a perfect gas

we have $\frac{\partial U}{\partial T}(\vec{r}(t)) = nC_V$, $\frac{\partial U}{\partial P}(\vec{r}(t)) = \frac{\partial U}{\partial V}(\vec{r}(t)) = 0$, thus $dU = (\frac{\partial U}{\partial T} \quad \frac{\partial U}{\partial P} \quad \frac{\partial U}{\partial V})$ gives

$$dU(\vec{r}(t)) \cdot \vec{r}'(t) = nC_V \frac{1}{nR} (V(t)P'(t) + P(t)V'(t)) + 0 + 0. \quad (6.32)$$

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

$$C_V \left(\frac{V(t)}{R} P'(t) + \frac{P(t)}{R} V'(t) \right) = -P(t)V'(t) \quad \text{along } \vec{r}, \quad (6.33)$$

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

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 body 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:

In a constant temperature cyclic transformation, no work can be created. (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

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

i.e. $dS(\vec{X}) \geq \frac{\delta Q(\vec{X})}{T}$. So, along any path $\vec{r} : t \in [t_0, t_f] \rightarrow \vec{X} = \vec{r}(t) \in \mathbb{R}^n$,

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

where $\Delta S = S(\vec{r}(t_f)) - S(\vec{r}(t_0))$.

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

$$dS = \frac{\delta Q}{T} \text{ along } \vec{r}, \quad (7.6)$$

in which case $\Delta S = \int_{\vec{r}} \frac{\delta Q}{T}$.

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

Example 7.4 $\delta W = -P dV$ gives $\delta Q = dU + P dV$. Consider a perfect gas: $dU = C_V dT$. And consider a reversible transformation. Hence

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

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 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

$$dU = T dS - P dV. \quad (7.8)$$

Thus it is “natural” to choose S and V as the “independent thermodynamic variables” for U : Thus

$$\frac{\partial U}{\partial S}|_V = T, \quad \frac{\partial U}{\partial V}|_S = -P. \quad (7.9)$$

Full notations: Define $\bar{U} : \mathbb{R}^2 \rightarrow \mathbb{R}$ by (up to a constant)

$$d\bar{U}(S, V) = \bar{T}(S, V) dS - \bar{P}(S, V) dV, \quad \text{so} \quad \frac{\partial \bar{U}}{\partial S}(S, V) = \bar{T}(S, V), \quad \frac{\partial \bar{U}}{\partial V}(S, V) = -\bar{P}(S, V). \quad (7.10)$$

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 the “independent thermodynamic variables” for S : Thus

$$\frac{\partial S}{\partial U}|_V = \frac{1}{T} \quad \text{and} \quad \frac{\partial S}{\partial V}|_U = \frac{P}{T}. \quad (7.12)$$

Full notations: Define $\underline{S} : \mathbb{R}^2 \rightarrow \mathbb{R}$ by (up to a constant)

$$d\underline{S}(U, V) = \frac{1}{\underline{T}(U, V)} dU + \frac{\underline{P}(U, V)}{\underline{T}(U, V)} dV, \quad \text{so} \quad \frac{\partial \underline{S}}{\partial U}(U, V) = \frac{1}{\underline{T}(U, V)}, \quad \frac{\partial \underline{S}}{\partial V}(U, V) = \frac{\underline{P}(U, V)}{\underline{T}(U, V)}. \quad (7.13)$$

Remark. Fix $V = V_0$ and write $S = \underline{S}_{V_0}(U) := \underline{S}(U, V_0)$ and $U = \bar{U}_{V_0}(S) := \bar{U}(S, V_0)$. 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.

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

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

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

8 Enthalpy, free energy, free enthalpy

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

Choose the independent thermodynamical variables to be S and P ; Thus the internal energy U and the enthalpy function $H = U + PV$ are characterized by

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

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

$$dH = T dS + V dP, \quad \text{and} \quad \frac{\partial H}{\partial S}|_P = T, \quad \frac{\partial H}{\partial P}|_S = V, \quad (8.2)$$

Full notations: $\delta W(S, P) = -P d\widehat{\mathcal{V}}(S, P)$ and

$$d\widehat{\mathcal{H}}(S, P) = \widehat{\mathcal{T}}(S, P) dS + \widehat{\mathcal{V}}(S, P) dP, \quad \text{i.e.} \quad \frac{\partial \widehat{\mathcal{H}}}{\partial S}(S, P) = \widehat{\mathcal{T}}(S, P), \quad \frac{\partial \widehat{\mathcal{H}}}{\partial P}(S, P) = \widehat{\mathcal{V}}(S, P). \quad (8.3)$$

Proof. Starting point: (7.9). So here $U = \widehat{\mathcal{U}}(S, P) = \overline{U}(S, V) = \overline{U}(S, \widehat{\mathcal{V}}(S, P))$, with $T = \overline{T}(S, V) = \frac{\partial \overline{U}}{\partial S}(S, V)$ and $P = \overline{P}(S, V) = -\frac{\partial \overline{U}}{\partial V}(S, V)$, cf. (7.9). Thus

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

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 $V \leftrightarrow P$ implicitly used to obtain $\widehat{\mathcal{U}}(S, P)$ from $\widehat{\mathcal{U}}(S, V)$ is in fact a Legendre transform.

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

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

which is what the Legendre transform does (when \overline{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)

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

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

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

Hence the “natural” variables are T and V , and then

$$\frac{\partial F}{\partial T}|_V = -S, \quad \frac{\partial F}{\partial V}|_T = -P. \quad (8.9)$$

Full notations: Define the free energy function $\tilde{F} : (T, V) \in \mathbb{R}^2 \rightarrow \mathbb{R}$ by (up to a constant)

$$d\tilde{F}(T, V) = -\tilde{S}(T, V) dT - \tilde{P}(T, V) dV, \quad \text{so} \quad \frac{\partial \tilde{F}}{\partial T}(T, V) = -\tilde{S}(T, V), \quad \frac{\partial \tilde{F}}{\partial V}(T, V) = -\tilde{P}(T, V). \quad (8.10)$$

Interpretation: For a reversible transformation at constant temperature:

$$dF = 0 - P dV = \delta W, \quad (8.11)$$

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

Exercice 8.3 With $\delta W = -P dV$ and a reversible transformation, express F with the Legendre transform $S \rightarrow T = \tilde{U}'_V(S)$ (slope of \tilde{U}_V at S). And get (8.10).

Answer. Starting point: variables S and V , so $d\tilde{U}(S, V) = \tilde{T}(S, V) dS - \tilde{P}(S, V) dV$, and $F = \tilde{F}(S, V) = \tilde{U}(S, V) - \tilde{T}(S, V)S$, with $F = \tilde{F}(T, V) = \tilde{F}(S, V)$, thus $\tilde{F}_V(T) = \tilde{F}_V(S)$ at any V : This is a change of variable $T \leftrightarrow S$, given by

$$T \stackrel{(7.9)}{=} \frac{\partial \tilde{U}}{\partial S}(S, V) = \tilde{U}'_V(S) = \text{slope of } \tilde{U}_V \text{ at } S: \text{ Legendre transform.} \quad (8.12)$$

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

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

$$\begin{cases} \frac{\partial \tilde{F}}{\partial T}(T, V) = \frac{\partial \tilde{U}}{\partial S}(\tilde{S}(T, V), V) \frac{\partial \tilde{S}}{\partial T}(T, V) - \tilde{S}(T, V) - T \frac{\partial \tilde{S}}{\partial T}(T, V) \stackrel{(8.12)}{=} -\tilde{S}(T, V), \\ \frac{\partial \tilde{F}}{\partial V}(T, V) = \frac{\partial \tilde{U}}{\partial S}(\tilde{S}(T, V), V) \frac{\partial \tilde{S}}{\partial V}(T, V) + \frac{\partial \tilde{U}}{\partial V}(\tilde{S}(T, V), V) - T \frac{\partial \tilde{S}}{\partial V}(T, V) \stackrel{(8.12)}{=} \frac{\partial \tilde{U}}{\partial V}(\tilde{S}(T, V), V). \end{cases} \quad (8.13)$$

And $P \stackrel{(7.9)}{=} -\frac{\partial \tilde{U}}{\partial V}(S, V) = \tilde{P}(S, V) = \tilde{P}(\tilde{S}(T, V), V) = \tilde{P}(T, V)$, thus (8.10). ▀

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

The free enthalpy G is

$$G := H - TS \quad (= U + PV - TS). \quad (8.14)$$

With a reversible transformation and $\delta W = -P dV$, we have $dU = T dS - P dV$, thus

$$\begin{aligned} dG &= (T dS - P dV) + (V dP + P dV) - (S dT + T dS) \\ &= V dP - S dT. \end{aligned} \quad (8.15)$$

Thus the “natural” variables are T and P and

$$dG = V dP - S dT, \quad \frac{\partial G}{\partial T}|_P = -S, \quad \frac{\partial G}{\partial P}|_T = V. \quad (8.16)$$

Full notations:

$$G = \hat{G}(T, P) \stackrel{(8.14)}{=} \hat{H}(T, P) - T \hat{S}(T, P), \quad \text{so} \quad \frac{\partial \hat{G}}{\partial T}(T, P) = -\hat{S}(T, P), \quad \frac{\partial \hat{G}}{\partial P}(T, P) = \hat{V}(T, P). \quad (8.17)$$

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.)

Exercise 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

$$\frac{\partial G}{\partial T}(T, P) := \frac{\partial z}{\partial T}(T, P) = -\frac{H(S(T, P), P)}{T^2} + \frac{1}{T} \frac{\partial H}{\partial S}(S(T, P), P) \frac{\partial S}{\partial T}(T, P) - \frac{\partial S}{\partial T}(T, P), \quad (8.18)$$

with $\frac{\partial H}{\partial S}(S(T, P), P) = T$, cf. (8.3). ▀

9 Gibbs–Duhem equations

Here S and V are the chosen variables. The internal energy being extensive, $\bar{U}(\lambda \vec{X}) = \lambda \bar{U}(\vec{X})$, i.e. $\bar{U}(\lambda S, \lambda V) = \lambda \bar{U}(S, V)$, 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 a reversible transformation, and $\delta W = -P dV$, together with $\frac{\partial \bar{U}}{\partial S}(S, V) = \bar{T}(S, V)$ and $\frac{\partial \bar{U}}{\partial V}(S, V) = -\bar{P}(S, V)$ cf. (7.9), give

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

Thus $dU = T dS + S dT - P dV - V dP$, with $dU = T dS - P dV$, thus

$$S dT - V dP = 0. \quad (9.3)$$

Thus $S \left(\frac{\partial T}{\partial S} \Big|_V dS + \frac{\partial T}{\partial V} \Big|_S dV \right) - V \left(\frac{\partial P}{\partial S} \Big|_V dS + \frac{\partial P}{\partial V} \Big|_S dV \right) = 0$, hence

$$S \frac{\partial T}{\partial S} \Big|_V - V \frac{\partial P}{\partial S} \Big|_V = 0 \quad \text{and} \quad S \frac{\partial T}{\partial V} \Big|_S - V \frac{\partial P}{\partial V} \Big|_S = 0 \quad (\text{Gibbs–Duhem equations}). \quad (9.4)$$

Full notation: $\bar{U}(S, V) = S \bar{T}(S, V) - V \bar{P}(S, V)$ gives $\frac{\partial \bar{U}}{\partial S} = \bar{T} + S \frac{\partial \bar{T}}{\partial S} - V \frac{\partial \bar{P}}{\partial S}$ and $\frac{\partial \bar{U}}{\partial V} = S \frac{\partial \bar{T}}{\partial V} - \bar{P} - V \frac{\partial \bar{P}}{\partial V}$, together with $\frac{\partial \bar{U}}{\partial S} = \bar{T}$ and $\frac{\partial \bar{U}}{\partial V} = -\bar{P}$, thus $S \frac{\partial \bar{T}}{\partial S} - V \frac{\partial \bar{P}}{\partial S} = 0$ and $S \frac{\partial \bar{T}}{\partial V} - V \frac{\partial \bar{P}}{\partial V} = 0$, at any $\vec{X} = (S, V)$.

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

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

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

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

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

Exercice 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 $\frac{\partial g}{\partial y}(x, y) = 0 + \frac{\partial f}{\partial Y}(\lambda x, \lambda y)\lambda \stackrel{\text{noted}}{=} \frac{\partial f}{\partial(\lambda y)}(\lambda x, \lambda y)\lambda$. ■

Exercice 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 $g'(x) = \int_{t=0}^x \frac{\partial f}{\partial x}(x, t) dt + f(x, x)$. ■

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., for all \vec{x} , 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 . ■

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

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

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

(Recall: $\partial_1 f(\vec{X}) := \lim_{h \rightarrow 0} \frac{f(X_1+h, X_2, \dots) - f(X_1, X_2, \dots)}{h} \stackrel{\text{noted}}{=} \frac{\partial f}{\partial X_1}(X_1, \dots, X_n)$, So $\partial_1 f(\lambda \vec{x}) = \lim_{h \rightarrow 0} \frac{f(\lambda x_1+h, \lambda x_2, \dots) - f(\lambda x_1, \lambda x_2, \dots)}{h} \stackrel{\text{noted}}{=} \frac{\partial f}{\partial(\lambda x_1)}(\lambda x_1, \lambda x_2, \dots)$, idem for all X_i .)

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

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

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: $\frac{\partial x}{\partial y} \frac{\partial y}{\partial x} = 1$

(This is nothing more than $(f^{-1} \circ f)(x) = x$ which gives $(f^{-1})'(f(x)) \cdot f'(x) = 1$, written $\frac{dx}{dy} \frac{dy}{dx} = 1$, when $f : x \rightarrow y = f(x)$ is a diffeomorphism.)

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

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

And $\frac{df_2}{dx}(x) \frac{df_1}{dy}(y) = 1$, written $\frac{dy}{dx} \frac{dx}{dy} = 1$.

Proof. Apply the implicit function theorem (since Z is C^2 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 C^1 functions f_1 and f_2 s.t. $f_1 \circ f_2 = I$ exist, thus $x = (f_1 \circ f_2)(x)$, 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 $f_1'(P) f_2'(T) = 1$ when $P = f_2(T)$, 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 $y = f_2(x, z_3, \dots, z_n) \stackrel{\text{noted}}{=} f_{2, z_3, \dots, z_n}(x)$, $x = f_1(y, z_3, \dots, z_n) \stackrel{\text{noted}}{=} f_{1, z_3, \dots, z_n}(y)$ and (C.2) gives

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

Thermodynamic notation:

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

Example C.3 Perfect gas: $Z(T, P, V, n) = PV - nRT$. Thus $P = f_2(T, V, n) = \frac{nR}{V} T$ and $T = f_1(P, V, n) = \frac{V}{nR} P$. We check: $(f_2 \circ f_1)(T, V, n) = \frac{nR}{V} (\frac{V}{nR} T) = T$ 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 $i \in [1, 3]_{\mathbb{N}}$ and $x_i \in \{x, y, z\}$, then $\exists f_1, f_2, f_3 \in C^1(\mathbb{R}^2; \mathbb{R})$ s.t.*

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

(Circular permutation for the variables.)

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

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:

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