

CHAPTER 1

Relevant Mathematics and Thermodynamics

Mathematics provides a convenient framework to describe many phenomena in physical chemistry (and physics and ... and ...). In this chapter the main mathematical techniques required for this course are recapped. Note that the mathematics here should be considered as a ‘*tool*’ to describe the physical chemistry of liquids and solutions and not as a goal on its own. Similarly, many results from classical thermodynamics will be used throughout the course. The most relevant thermodynamics will also be recapped in this chapter.

1.1. Relevant mathematics

1.1.1. Taylor’s expansion. In 1715 Brooke Taylor (English mathematician, 1685-1731) published his famous theorem, which states that a (complicated) function can be expressed as a polynomial, i.e. as a sum of powers of the relevant variable. Often the behaviour of the function around its origin is already sufficient to describe diluted systems. Higher order terms provide corrections to that and can be included to describe more concentrated systems.

Taylor’s expansion is defined as

$$\begin{aligned} f(x) &= f(0) + \left(\frac{df}{dx}\right)_{x=0} x + \frac{1}{2} \left(\frac{d^2f}{dx^2}\right)_{x=0} x^2 + \frac{1}{6} \left(\frac{d^3f}{dx^3}\right)_{x=0} x^3 + \dots \\ &= \sum_{n=0}^{\infty} \frac{x^n}{n!} \left(\frac{d^n f}{dx^n}\right)_{x=0}. \end{aligned} \quad (1.1)$$

Here, $\left(\frac{d^n f}{dx^n}\right)_{x=0}$ is the n -th derivative of the function f with respect to x , evaluated at the origin. The summation $\sum_{n=0}^{\infty}$ indicates a series for which the variable n runs from zero to infinity. Similarly, a product can be written as $\prod_{n=0}^{\infty}$ and consequently the faculty as

$$n! = \prod_{i=1}^n i = n \cdot (n-1) \cdot \dots \cdot 2 \cdot 1, \quad (1.2)$$

with $0! \equiv 1$.

Popular Taylor's expansions. Taylor's expansions which are often used

$$e^x = 1 + x + \frac{1}{2}x^2 + \dots$$

$$\ln(1 + x) = x - \frac{1}{2}x^2 + \dots$$

$$(1 + x)^n = 1 + nx + \frac{1}{2}n(n-1)x^2 + \dots$$

The expansions are up to 2^{nd} order, i.e. up to x^2 .

1.1.2. Total differential. In thermodynamics one often encounters total differentials.

The total differential of a function f defined by n variables x_1, x_2, \dots, x_n is given by

$$\begin{aligned} df &= \left(\frac{\partial f}{\partial x_1} \right)_{x_2, x_3, \dots, x_n} dx_1 + \left(\frac{\partial f}{\partial x_2} \right)_{x_1, x_3, \dots, x_n} dx_2 + \dots + \left(\frac{\partial f}{\partial x_n} \right)_{x_1, x_2, \dots, x_{n-1}} dx_n \\ &= \sum_{i=1}^n \left(\frac{\partial f}{\partial x_i} \right)_{x_j \neq i} dx_i. \end{aligned} \quad (1.3)$$

The 'straight' d describes the total change of a function or a variable. The 'curved' ∂ corresponds to the partial change. The term $\left(\frac{\partial f}{\partial x_i} \right)_{x_j \neq i}$ describes the change of f as a function of a change in x_i while all other variables $j \neq i$ are constant. So the total change in f due to a change in x_i also depends on how the other variables change:

$$\frac{df}{dx_1} = \left(\frac{\partial f}{\partial x_1} \right)_{x_2, x_3, \dots, x_n} + \sum_{i=2}^n \left(\frac{\partial f}{\partial x_i} \right)_{x_j \neq i} \frac{dx_i}{dx_1}.$$

Thermodynamic definitions. In section 1.2 we will see that the change in the Helmholtz free energy can be written as

$$dA = -SdT - PdV + \sum_{i=1}^c \mu_i dn_i.$$

The Helmholtz free energy is a function of the temperature T , the volume V and the number of moles n_i of each component c . If the Helmholtz free energy is solely a function of these variables, $A = A(T, V, n_1, \dots, n_c)$, the total differential is given by

$$dA = \left(\frac{\partial A}{\partial T} \right)_{V, n'_i, s} dT + \left(\frac{\partial A}{\partial V} \right)_{T, n'_i, s} dV + \sum_{i=1}^c \left(\frac{\partial A}{\partial n_i} \right)_{T, V, n_j \neq i} dn_i.$$

Comparing these expression for the change of the Helmholtz free energy, we find

$$\left(\frac{\partial A}{\partial T} \right)_{V, n'_i, s} = -S, \quad \left(\frac{\partial A}{\partial V} \right)_{T, n'_i, s} = -P, \quad \left(\frac{\partial A}{\partial n_i} \right)_{T, V, n_j \neq i} = \mu_i.$$

This means, e.g. for the last expression, that the change in Helmholtz free energy due to a change in the number of moles of component i at constant temperature, volume and number of moles of the other components, is given by the chemical potential of component i .

A total differential has two important properties. The first one is that the order of differentiation is unimportant

$$\left(\frac{\partial}{\partial x_i} \left(\frac{\partial f}{\partial x_j} \right)_{x_i \neq j} \right)_{x_j \neq i} = \left(\frac{\partial}{\partial x_j} \left(\frac{\partial f}{\partial x_i} \right)_{x_j \neq i} \right)_{x_i \neq j}. \quad (1.4)$$

The second one is that if we integrate over a closed path and thus return in the initial state, the result equals zero.

$$\oint df = 0. \quad (1.5)$$

Maxwell-relations. If the above differential of the Helmholtz free energy is total, then

$$\left(\frac{\partial \mu_i}{\partial V} \right)_{T, n'_i s} = \left(\frac{\partial}{\partial V} \left(\frac{\partial A}{\partial n_i} \right)_{T, V, n_j \neq i} \right)_{T, n'_i s} = \left(\frac{\partial}{\partial n_i} \left(\frac{\partial A}{\partial V} \right)_{T, n'_i s} \right)_{T, V, n_j \neq i} = - \left(\frac{\partial P}{\partial n_i} \right)_{T, V, n_j \neq i}.$$

This is one of the Maxwell-relations that states that the change in the chemical potential of component i as a function of the volume at constant temperature and number of moles equals the change of the pressure if we change the number of moles of component i at constant temperature, volume and number of moles of the other components.

The second condition the total differential of the Helmholtz free energy has to obey is

$$\oint dA = 0,$$

which implies that the change in the Helmholtz free energy is zero if we return in the initial state. In other words, the Helmholtz free energy is uniquely defined by the temperature, the volume and the number of moles in that state. Recall that this is a general property of a state function.

1.1.3. Homogeneous functions. A function f is homogeneous if

$$f(ax_1, ax_2, \dots, ax_n) = af(x_1, x_2, \dots, x_n).$$

In other words, if the variables become a factor a larger, then the function f also becomes a times as large. In thermodynamics such quantities are termed as *extensive*. For example, the number of particles is an extensive quantity: if we merge a identical subsystems, the total number of particles in the total system has also increased by a factor a . The temperature of the total system however will not change with the number of identical subsystems. Such quantities are termed *intensive* variables.

If a function is homogeneous (extensive) with respect to the variables x_1, x_2, \dots, x_n , Euler's equation states that f can be written as

$$f = \sum_{i=1}^n \left(\frac{\partial f}{\partial x_i} \right)_{x_j \neq i} x_i. \quad (1.6)$$

Helmholtz free energy. The Helmholtz free energy is function of the temperature, the volume and the number of moles of each component i ; $A = A(T, V, n'_i s)$ and the total differential is given by

$$\begin{aligned} dA &= \left(\frac{\partial A}{\partial T} \right)_{V, n'_i s} dT + \left(\frac{\partial A}{\partial V} \right)_{T, n'_i s} dV + \sum_{i=1}^c \left(\frac{\partial A}{\partial n_i} \right)_{T, V, n_j \neq i} dn_i \\ &= -SdT - PdV + \sum_{i=1}^c \mu_i dn_i. \end{aligned}$$

Because the Helmholtz free energy is extensive with respect to the volume V and the number of moles n_i , we can apply Euler, eq (1.6), and write

$$\begin{aligned} A &= \left(\frac{\partial A}{\partial V} \right)_{T, n'_i s} V + \sum_{i=1}^c \left(\frac{\partial A}{\partial n_i} \right)_{T, V, n_j \neq i} n_i \\ &= -PV + \sum_{i=1}^c \mu_i n_i. \end{aligned}$$

Note that the term $-ST$ is not present in the Helmholtz free energy. Physically this can be understood as follows: by integrating over $-SdT$, no ‘infinitesimal amounts of temperature’ are added and hence this term does not show up in the Helmholtz free energy. In contrast, the integral over $-PdV$ means that we are adding infinitesimal small amounts of volume, which in total leads to the term $-PV$ in the Helmholtz free energy. Analogous, the number of moles of each component add up to the term $\sum_{i=1}^c \mu_i n_i$. In section 1.2 we will see that integrating over the change in the internal energy dU and applying the definition of the Helmholtz free energy, $A \equiv U - TS$, indeed leads to the above equation.

1.2. Relevant thermodynamics

Thermodynamics describes how heat and work can be converted into each other and is based on two empirical relations which have never been found to be false. In the following these laws of thermodynamics will be briefly described.

1.2.1. First law of thermodynamics. The first law of thermodynamics was first formulated by Helmholtz in 1847, who argued that the energy of a system can only be changed by the addition or (the opposite of addition) of heat and work. In 1865 Clausius formulated this mathematically as:

$$dU = \vec{\delta}q + \vec{\delta}w \quad \text{‘Die Energie der Welt ist konstant’}. \quad (1.7)$$

U is the internal energy of the system, q the added heat and w the work done on the systems. The bars ($\vec{\delta}$ ’s) indicate that these are not total differentials.

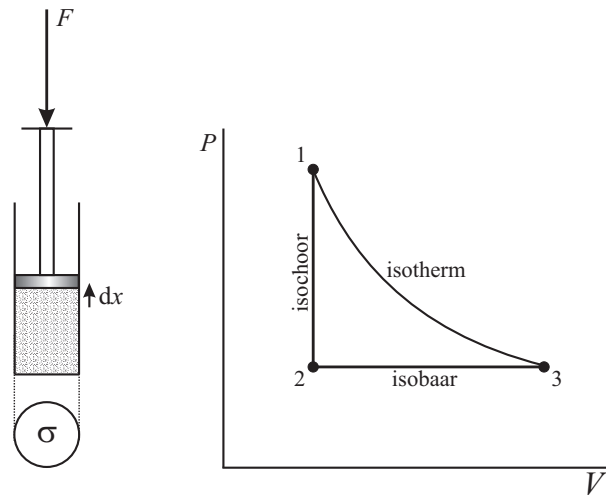


FIGURE 1.1. The expansion work PdV done by the piston along the isotherm from point $1 \rightarrow 3$ is different from the work done via the isochoric plus isothermal ($1 \rightarrow 2 \rightarrow 3$) path; dw is not a state function.

This can be easily understood by considering a piston filled with gas as indicated in figure 1.1. If we assume that the piston has no mass and friction is neglected, the work to move the piston over a small distance dx is

$$\vec{d}w = Fdx = -P\sigma dx = -PdV, \quad (1.8)$$

where F is the required force. The opposing force comes from the pressure P of the gas, which is a force per unit area. The force is exerted on an area σ , so σdx is the change in the volume dV . Changing the piston from the initial position at pressure P_1 and volume V_1 to a lower pressure P_3 and larger volume V_3 can be achieved in many ways; see figure 1.1. One possibility is to do this isothermally; the corresponding work is graphically represented by the area under the isotherm $1 \rightarrow 3$ in figure 1.1; $w_{1 \rightarrow 3} = -\int_1^3 PdV$. Another possible path is to first lower the pressure at constant volume (isochore) and then increase the volume at constant pressure (isobar). The work is again represented by the total area under the isochore ($1 \rightarrow 2$) and the isobar ($2 \rightarrow 3$). It is obvious that $w_{1 \rightarrow 3} \neq w_{1 \rightarrow 2} + w_{2 \rightarrow 3}$. In other words, for the full cycle $1 \rightarrow 2 \rightarrow 3 \rightarrow 1$ the total work is given by the enclosed area, which immediately implies that

$$\oint \vec{d}w \neq 0.$$

As this is not consistent with eq (1.5), $\vec{d}w$ is not a total differential and work is therefore not a state function. The first law of thermodynamics states that the internal energy is constant, so if we come back to the initial state

$$\oint dU = 0.$$

Hence, dU and U are respectively a total differential and a state function. It then follows immediately from eq (1.7) that heat cannot be a state function either and that $\vec{a}q$ is not a total differential.

To ensure that the internal energy is a total differential, all variables that determine the internal energy should be taken into account; no less, but also no more. In the example of the (frictionless \rightarrow no heat) piston, the internal energy was only determined by expansion-work. However, this is only one example of work. If the piston in some way would also be able to exchange matter with the surroundings, the change in matter, dn_i , also contributes to the internal energy. This is another source of work. Just as expansion work, required to change the volume, is coupled to the pressure $-PdV$, the work required to change the number of moles (or particles) of component i is coupled to the chemical potential ($\mu_i dn_i$). So for an ‘open’ system the total change of work can be expressed as

$$\vec{a}w = -PdV + \sum_{i=1}^c \mu_i dn_i + \dots, \quad (1.9)$$

where the dots correspond to other possible types of work. For example, later we will see that in a system consisting of two phases, the interface between the phases will also contribute to the internal energy of the system, which gives rise to yet another type of work.

1.2.2. Second law of thermodynamics. Though the first law exactly describes what the change in the internal energy of a given process is, it does not say anything about the direction of that process. To complete the thermodynamic toolkit we introduce a new state function that provides this information: the entropy S , which couples the temperature to heat (just as the volume couples the pressure to expansion work).

$$\vec{a}q = TdS \quad \rightarrow \quad dS = \frac{\vec{a}q}{T}. \quad (1.10)$$

How does the entropy S determine the direction of a process? Consider again the piston filled with a gas in figure 1.1. Now we follow a reversible adiabatic path from 1 to 3, i.e. infinitesimal small, reversible steps are taken without exchanging heat: $\vec{a}q = 0$. From the First Law, eq (1.7), it then follows that the change in the internal energy is $\Delta U = w_{\text{rev}}$. We also know that the amount of work done is at its maximum for a reversible process. Because the internal energy does not depend on the path chosen (it is a state function), heat must be added for any irreversible path that also leads from 1 to 3: $\Delta U = w_{\text{rev}} = q_{\text{irr}} + w_{\text{irr}}$, in other words $q_{\text{irr}} = w_{\text{rev}} - w_{\text{irr}}$. As w_{rev} always corresponds to the maximum amount of work, we conclude that $q \geq 0$. Since the temperature is

always positive, eq (1.10) leads to

$$dS \geq \frac{\delta q}{T} \quad (1.11)$$

This is the Second law of thermodynamics, which was formulated in 1865 by Clausius as

$$\Delta S \geq 0 \quad \text{‘Die Entropie der Welt strebt ein Maximum zu’}.$$

The Second law indicates the direction of a process, i.e. towards the state of maximum entropy.

1.2.3. Combining the laws of thermodynamics: equilibrium. Substituting the expressions for the heat, eq (1.10), and the work, eq (1.9), in the first law (eq (1.7)) leads to

$$dU = TdS - PdV + \sum_{i=1}^c \mu_i dn_i. \quad (1.12)$$

Using the second law, eq (1.11), then leads to

$$dS \geq \frac{1}{T}dU + \frac{P}{T}dV - \sum_{i=1}^c \frac{\mu_i}{T}dn_i.$$

If we were to do a process at constant entropy, volume and number of moles (i.e. number of particles), we see that the internal energy is minimized: $dU \leq 0$. In equilibrium the internal energy of the system is at its minimum.

If the volume and the number of moles (particles) are the only terms that can change the work, the change in internal energy (eq (1.12)) is a total differential. The pressure is thermodynamically defined as: $P = -\left(\frac{\partial U}{\partial V}\right)_{S, n_i}$, which implies that we have to measure the change in the internal energy at constant entropy and number of moles to obtain the pressure. Especially, the first condition, constant entropy, is experimentally hard to realise. It would be much easier to work at constant temperature. To describe such a process, we have to change the variable S to the variable T using a so-called Legendre-transformation. The internal energy is now changed to the Helmholtz free energy:

$$A \equiv U - TS \quad \Rightarrow \quad dA = dU - TdS - SdT$$

$$dA = -SdT - PdV + \sum_{i=1}^c \mu_i dn_i. \quad (1.13)$$

Using $A = A(T, V, n_i)$, we see that the pressure now follows from: $P = -\left(\frac{\partial A}{\partial V}\right)_{T, n_i}$, which is experimentally easier to determine. So, for a process at constant temperature, volume and number of moles, the system is in equilibrium at a minimum of the Helmholtz free energy: $dA \leq 0$.

The Helmholtz free energy again. The internal energy is extensive in S , V and n_i 's. Integration of the homogeneous function eq (1.12) leads to

$$U = TS - PV + \sum_{i=1}^c \mu_i n_i.$$

By applying the definition of the Helmholtz free energy we obtain

$$A \equiv U - TS = -PV + \sum_{i=1}^c \mu_i n_i.$$

This also illustrates why A is a 'free' energy; it corresponds to that part of the internal energy that is available for work.

Gibbs-Duhem equation. In the previous paragraph we have seen that we can apply Euler's theorem eq (1.6) to write the Helmholtz free energy as

$$A = -PV + \sum_{i=1}^c \mu_i n_i.$$

If we differentiate this expression again we obtain

$$dA = -PdV - VdP + \sum_{i=1}^c \mu_i dn_i + \sum_{i=1}^c n_i d\mu_i.$$

Now subtracting the total differential of the Helmholtz free energy eq (1.13) from above equation leads to

$$0 = SdT - VdP + \sum_{i=1}^c n_i d\mu_i \quad \implies \quad \sum_{i=1}^c n_i d\mu_i = -SdT + VdP,$$

which is called the Gibbs-Duhem equation. For a single component this reduces to

$$d\mu_i = -\bar{s}dT + \bar{v}dP,$$

where \bar{s} and \bar{v} are respectively the molar entropy and molar volume.

The physical interpretation of the chemical potential can also be derived from eq (1.13)

$$\mu_i = \left(\frac{\partial A}{\partial n_i} \right)_{T, V, n_{j \neq i}}. \quad (1.14)$$

The chemical potential is thus the work required to add a mole of particles of component i at constant temperature, volume and number of moles of other components. Therefore, the chemical potential represents chemical work. In equilibrium the work to extract a particle of type i from phase α must be equal to the work required to insert that same particle into phase β and the other way around. Mathematically, this chemical equilibrium is expressed as

$$\mu_i^\alpha = \mu_i^\beta. \quad (1.15)$$

We will use this condition for chemical equilibrium many times throughout this course.

1.2.4. Boltzmann's equation. Boltzmann was the first to realise that the thermodynamic quantity 'entropy', S , is directly related to number of microscopic realisations, Ω . When we merge two systems A and B, the total entropy is the sum of the entropies of the two subsystems (entropy is extensive):

$$S = S^A + S^B.$$

The number of possibilities to realise a given configuration is proportional to the chance that the system is that particular configuration or state. When two systems are added together, the number of possible realisations will be the product of the Ω 's of the two individual systems

$$\Omega = \Omega^A \cdot \Omega^B.$$

The logarithm provides a natural way to couple these because

$$S \propto \ln \Omega = \ln \Omega^A \cdot \Omega^B = \ln \Omega^A + \ln \Omega^B = S^A + S^B.$$

The constant of proportionality is termed Boltzmann's constant

$$S = k_B \ln \Omega. \tag{1.16}$$

Note that this is a way to justify above Boltzmann's equation, rather than a strict derivation of it.