



GENERAL EQUATIONS OF PHYSICO-CHEMICAL PROCESSES

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Causes and conditions for the evolution of a system

Time evolution (or advance or progress) of a material system is dictated by two possible causes:

- Internal, due to initial conditions of non-equilibrium.
- External, due to boundary conditions of non-equilibrium.

Time evolution is constrained by some restrictions (laws of Nature), best expressed for an isolated system (be it considered a continuum or an ensemble of particles) as:

- In every real evolution of an isolated system, there is a state function called entropy, $S = \sum S_k(U_k, V_k, n_{ik})$, measuring the internal distribution of the conservative functions, that increases with time, $dS/dt > 0$ ($= 0$ only in the state of equilibrium). As a consequence of equilibrium, the sensitivity of that function to the independent variables cannot be different from one place to the other and, in absence of external fields, temperature, pressure, and the chemical potential, μ_i , of each chemical species i , must be uniform within the system. The fundamental equation that relates all constitutional variables at equilibrium is:

$$dS = \frac{1}{T} dU + \frac{p}{T} dV - \sum_{i=1}^c \frac{\mu_i}{T} dn_i \quad (0)$$

where temperature T measures the 'escaping force' of thermal energy, pressure p measures the 'escaping force' of mechanical energy, and the chemical potential μ_i measures the 'escaping force' of chemical energy. As a consequence of the tendency to equilibrium, it can be demonstrated that some variables and material properties are bounded (e.g. at equilibrium $T > 0$, $p > 0$, $c_p > 0$, $c_v > 0$, $c_p > c_v$, $\kappa > 0$, and during evolution $k > 0$, $\mu > 0$, $D_i > 0$), and, from the bunch of properties and functions used (ρ , p , T , u , h , s , etc.), only a few can be independently changed (e.g. only two, for simple compressible system), the others becoming functions of these variables.

- In every real evolution of an isolated system, one can find conservative components, $n_i = \sum n_{ik}$ (molecules in physical evolutions, atoms in chemical evolutions, more elementary particles in nuclear evolutions), such that $dn_i/dt = 0$ for every species i . Sometimes, this law is replaced by mass conservation, i.e. $dm_i/dt = 0$, with $m_i = M_i n_i$ and M_i being the molar mass of species i . Mass is so little variant with atomic interactions that it can be taken as a constant; in reality, it is always $\Delta m = \Delta E/c^2$, but $\Delta m \ll m$ in most interactions.

3. In every real evolution of an isolated system, there is a state function called (linear) momentum, $\vec{p} = \sum m_k \vec{v}_k$, which does not change with time.
4. In every real evolution of an isolated system, there is a state function called angular momentum, $\vec{L} = \sum \vec{r}_k \times m_k \vec{v}_k$, which does not change with time. This law becomes redundant if the previous one is applied to infinitesimal parts of the system, as done in a continuum.
5. In every real evolution of an isolated system, there is a state function called energy, E , measuring all internal motions and interactions in a certain integral way, independent of the origin of time, which does not change with time.
6. In every real evolution of an isolated system, the total electric charge does not change with time. But we disregard electric and magnetic effects altogether.

These universal laws for an isolated system can be grouped as:

- Conservation laws: there are a few magnitudes (according to Noether's theorem of correspondence between continuous symmetries and conservation laws), let us name them as Φ , which cannot change with time in isolated systems, i.e. $d\Phi/dt=0$.
- Equilibrium laws: after sufficient time, all magnitudes of an isolated system distribute in just one manner, called equilibrium distribution, such that the entropy function gets a maximum value, which for a single-phase system in absence of external forces implies that all magnitudes (mass, species, energy, speed) distribute uniformly, i.e. $d\Phi/d\vec{x} = 0$.
- Kinetic laws: in the evolution, the rate of change of a magnitude is proportional to the dis-equilibrium amount; e.g. the flux of thermal energy is proportional to the temperature gradient.
- Constitutive laws, relating the equilibrium and kinetic properties of matter (e.g. density, thermal capacity, conductivity, viscosity...) to the macroscopic state of a system.

For non-isolated systems, these universal laws are expressed in the form of balance equations, ascribing every input to the following common-language budgetary terms: accumulation, production (generation-consumption), or flux (input-output), such that accumulation \equiv production + net flux in, either in integral form (amounts) or in differential form (rates of change). Conservative magnitudes are those without internal production term (all of them may be conservative, except for entropy and its derived functions).

Integral formulation of balance equations

For a control mass, i.e. a closed system, impermeable to matter but permeable to energy:

$$\begin{array}{llll} \text{Magnitude} & \text{accumulation} & \text{production} & \text{(diffusive) flux} \\ \text{mass (total)} & \frac{dm}{dt} & = & 0 \quad +0 \end{array} \quad (1)$$

$$\begin{array}{llll} \text{species mass} & \frac{dm_i}{dt} & = & \dot{m}_{i,gen} \quad +0 \end{array} \quad (2)$$

$$\begin{array}{llll} \text{momentum} & \frac{d(m\vec{v})}{dt} & = & m\vec{g} \quad \int \vec{f}dA \end{array} \quad (3)$$

$$\text{energy} \quad \frac{d(me)}{dt} = \dot{E}_{gen} - \int \vec{q} \cdot \vec{n} dA + \int \vec{f} \cdot \vec{v} dA \quad (4)$$

$$\text{entropy} \quad \frac{d(ms)}{dt} = \dot{S}_{gen} - \int \frac{\vec{q} \cdot \vec{n}}{T} dA \quad (5)$$

In (2), a mass-production term has being included, $\dot{m}_{i,gen}$, namely the mass production of species i inside the system by chemical reactions (it can be the source or sink, cancelling in the whole, and it is usually related to other variables by means of Arrhenius' law, see below).

In (3), a momentum-production term has being included, $m\vec{g}$, due to the effect of an external volumetric force field (represented as a constant gravity field), and \vec{f} is the external force per unit area at the frontier.

In (4), an energy-production term has being included, \dot{E}_{gen} , as a convenient term to separately account for changes in internal energy of non-thermal origin, like mechanical dissipation by viscosity, electrical dissipation by Joule effect, chemical dissipation, phase changes, mixing enthalpy, etc.), and \vec{q} is the energy flux in the frontier due to a temperature difference (the heat transfer by molecular diffusion (and electrons flow in metals), and it is usually related to other variables by means of Fourier's law, see below).

In (5), the entropy-generation term, \dot{S}_{gen} , is an unknown in real processes. It is assume to be zero in the thermodynamic limit of ideal non-dissipating processes, and can be computed in terms of the transport coefficients and the detailed internal evolution. It can be empirically computed with Eq. (5) if all other variables are measured. Besides, for preliminary design purposes, this entropy production term can be approximated if data from similar processes allow a generic behaviour in terms of isentropic efficiencies (empirical ratios between real and ideal processes).

To pass from this control-mass formulation to one for open systems, first the model of a continuum system (field variables) is introduced, and then use is made of two mathematical theorems: the Reynolds Transport Theorem to pass from a closed system entrained by the flow to a permeable system, $d\Phi_{CM}/dt = \int_V (\partial\Phi/\partial t) dV + \int_A \Phi (\vec{v} - \vec{v}_A) \cdot \vec{n} dA$, and the Gauss-Ostrogradski Theorem to transform surface integrals at the boundary into volume integrals in the domain, $\int_A \Psi \otimes \vec{n} dA = \int_V \nabla \otimes \Psi dV$. All integrals now being volume integrals, they are applied to a generic elemental volume and one gets what the typical Eulerian description of the system, where every function, e.g. $T(\vec{x}, t)$, represents the value of temperature at position \vec{x} and any time t , although in some cases it may be convenient to use a Lagrangian description of the system, $T(\vec{x}(\vec{x}_0, t), t)$, where variables refer to moving material particles (moving with the flow).

Differential formulation of balance equations

For a unit control volume, at every point in the spatial domain bounding the system:

$$\begin{array}{ccccc} \text{Magnitude} & \text{accumulation} & \text{production} & \text{diffusive flux} & \text{convective flux} \\ \text{mass} & \frac{\partial \rho}{\partial t} & = & 0 & +0 & -\nabla \cdot (\rho \vec{v}) \end{array} \quad (6)$$

$$\text{species} \quad \frac{\partial \rho_i}{\partial t} = w_i - \nabla \cdot \vec{j}_i - \nabla \cdot (\rho_i \vec{v}) \quad (7)$$

$$\text{momentum} \quad \frac{\partial(\rho \vec{v})}{\partial t} = \rho \vec{g} + \nabla \cdot \bar{\tau} - \nabla \cdot (\rho \vec{v} \vec{v}) \quad (8)$$

$$\text{energy} \quad \frac{\partial e}{\partial t} = \dot{e}_{gen} - \nabla \cdot \vec{q} + \nabla \cdot (\bar{\tau} \cdot \vec{v}) - \nabla \cdot (e \vec{v}) \quad (9)$$

$$\text{entropy} \quad \frac{\partial s}{\partial t} = \dot{s}_{gen} - \nabla \cdot \frac{\vec{q}}{T} - \nabla \cdot (s \vec{v}) \quad (10)$$

where ρ_i is the mass-density of species i (mass of species i per unit volume of mixture), although equivalent equations can be formulated in terms of the mass fraction, $y_i \equiv m_i/m$, the mol fraction, $x_i \equiv n_i/n$, or the concentration, $c_i \equiv n_i/V$, of the species i , all of them related by (M_i is the molar mass of species i):

$$y_i \equiv \frac{m_i}{m} = \frac{\rho_i}{\rho} = x_i \frac{M_i}{\sum x_i M_i} = M_i c_i \quad (11)$$

Other terms introduced in (6-10) are the stress tensor $\bar{\tau}$ (such that the force over an elementary area with external normal \vec{n} is:

$$\vec{f} = \bar{\tau} \cdot \vec{n} = -p \cdot \vec{n} + \bar{\tau}' \cdot \vec{n} \quad (12)$$

with p being pressure and $\bar{\tau}'$ the viscous part of $\bar{\tau}$. Besides, the densities for accumulated energy, e , for generated energy, \dot{e}_{gen} , for accumulated entropy, s , and for generated entropy, \dot{s}_{gen} , have been introduced. We insist that in reality there is no energy generation (energy is conservative) and \dot{e}_{gen} refers to variation in the internal energy not accounted for in e , where we only account for thermal energy.

Usually, for a simple system (single component), one takes as independent space-time variables the local velocity, local pressure and local temperature, $\vec{v}(\vec{x}, t)$, $p(\vec{x}, t)$, $T(\vec{x}, t)$ (and composition for compound systems), and all the other functions are related to the former by constitutive laws (equations of state, $\rho(T, p)$, $h(T, p)$, and transport equations, $\tau = \tau(\vec{v}, T, p)$, $\vec{q} = \vec{q}(\vec{v}, T, p)$, $\vec{v}_{di} = \vec{v}_{di}(\vec{v}, T, p)$, and $w_i = w_i(\vec{v}, T, p)$).

The energy balance is usually developed in terms of temperature (instead of energy), what yields, in absence of phase changes and reactions:

$$\begin{array}{ccccc} \text{Magnitude} & \text{accumulation} & \text{production} & \text{diffusive flux} & \text{convective flux} \\ \text{energy} & \rho c_p \frac{\partial T}{\partial t} & = \bar{\tau}' : \nabla \vec{v} + \alpha T \frac{Dp}{Dt} & - \nabla \cdot \vec{q} & - \rho c_p \vec{v} \cdot \nabla T \end{array} \quad (13)$$

that reads: the accumulation of thermal-enthalpy equals the thermal-enthalpy production due to friction and work input, plus the net heat conduction, plus the convected thermal-enthalpy (in absence of phase changes, species diffusion, and chemical reactions).

Boundary conditions

Of the utmost importance for the evolution of a system are the boundary conditions, since they usually are the main difference between one problem and another (the internal equations been always the same). In many cases, however, the boundary conditions are not directly prescribed, but must match those of a neighbour system. If $[\phi]=\phi_{\text{inner}}-\phi_{\text{outer}}$ represents the jump in the value of a generic function ϕ across the interface, the boundary conditions in the simplest case of a geometrical boundary without other physical properties (no possibility of accumulation and production of any magnitude at the interface), are:

<u>Magnitude</u>	<u>local equilibrium</u>	<u>no-flux condition</u>	
mass	$0 = [\mu]$	$0 = [\vec{v}]$	(14)

species	$0 = [\mu_i]$	$0 = [\rho D_i \nabla (y_i + c_s T)]$	(15)
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momentum	$0 = [\vec{v}]$	$0 = [\bar{\tau} \cdot \vec{n}]$	(16)
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energy	$0 = [T]$	$0 = [k \nabla T \cdot \vec{n}]$	(17)
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(where μ stands for the chemical potential), although there are cases where one has to consider a net flux of mass (e.g. ablative processes), a net flux of species (e.g. accumulation/depletion of tenso-active species at the interface), a net flux of momentum (e.g. a normal and tangential forces due to capillarity), a net flux of energy (e.g. energy deposition by solid friction at the interface, radiation absorption, interface stretching, etc.), and a net flux of entropy associated to the above processes or due to the modellisation (e.g. when one assumes uniform temperatures, but distinct at both sides, an entropy production term, $[(k \nabla T \cdot \vec{n})/T]$, must be added).

Constitutive relations

To complete the field equations one has to make explicit (either from empirism or from kinetic theory) the initial conditions, the boundary conditions, and the constitutive relations at equilibrium, which are:

- Thermal) equation of state: $\rho=\rho(p,T,y_i)$. As an example, the ideal gas equation of state:

$$\rho = \frac{p}{R_u T} \frac{1}{\sum \frac{y_i}{M_i}} \quad (18)$$

- Energetic equation of state: $h=h(p,T,y_i)$. As an example, the ideal gas enthalpy:

$$h = \sum y_i \left[h_i^\oplus + c_{p_i} (T - T^\oplus) \right] \quad (19)$$

- Chemical equations of state for each species except one: $\mu_i=\mu_i(p,T,y_i)$. As an example, for an ideal gas mixture:

$$\mu_i = \mu_i^\oplus (T, p^\oplus) + R_u T \ln \frac{p}{p^\oplus} + R_u T \ln \left(y_i \frac{M}{M_i} \right) \quad (20)$$

plus the constitutive relations for evolution (transport equations, that relate all diffusive fluxes to the forces that originate them, and chemical kinetics):

- Mass diffusion (generalised Fick's law with Soret effect):

$$\vec{j}_i = -D_i \nabla (\rho_i + c_s T / \rho) \quad (21)$$

- Momentum diffusion (Stokes' law):

$$\vec{\tau} = -p \vec{I} + \mu (\nabla \vec{v} + (\nabla \vec{v})^T) - \left(\frac{2}{3} \mu - \mu_v \right) (\nabla \cdot \vec{v}) \vec{I} \quad (22)$$

- Energy diffusion (generalised Fourier's law with species diffusion).

$$\vec{q} = -k \nabla T + \sum \rho_i \vec{v}_{di} h_i \quad (23)$$

- Chemical kinetics (Arrhenius' law):

$$w_i = M_i (v_i'' - v_i') \prod \left(\frac{\rho_j}{M_j} \right)^{v_j} B_a \exp \left(\frac{-E_a}{RT} \right) \quad (24)$$

where μ_i is the chemical potential for species i , D_i is the coefficient of mass diffusion due to concentration gradients, c_s is the Soret coefficient of mass diffusion due to thermal gradients, μ and μ_v are the dynamic viscosity coefficients (shear and volumetric), \vec{v}_{di} is the diffusion velocity such that $\rho_i \vec{v}_{di} = -D_i \nabla \rho_i$, w_i is the mass of species i produced by unit of mass of the mixture and time due to chemical reactions, v_i'' and v_i' the stoichiometric coefficients for the forward and backward reaction considered (multiples w_i must be considered for multiple reactions), and B_a and E_a two empirical Arrhenius coefficients.

The kinetic theory of gases provide a simple (although sometimes not very accurate) formulation of all the transport coefficients and equations of state in terms of pressure, temperature and composition, but in practice one usually resorts to tabulated experimental data.

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