Non-equilibrium Thermodynamics
Balance of mass and of entropy
Local equilibrium principle

Most of the real processes are non-equilibrium. Their direction is determined by the II law of Thermodynamics. For isolated system (not exchanging energy with the surrounding) $\dfrac{dS}{dt} \geq 0$

Second Postulate (temperature)
Every **equilibrium** system is completely determined by the set of external variables (volume, pressure, magnetic field, etc.) plus one internal variable – **TEMPERATURE.**
For nonequilibrium systems in addition to temperature some other internal variables $\boldsymbol{x}_i$ are needed.

Out of equilibrium some more internal parameters are needed in addition to temperature to describe the system

$$dG = -SdT + pdV - \sum_i A_i d\boldsymbol{x}_i$$

$$A_i = -\left(\frac{\partial G}{\partial \boldsymbol{x}_i}\right)_{P,T,\boldsymbol{x}_j} \quad \textbf{AFINITY}$$

Nemilov formulated a criterion that two order parameters $\boldsymbol{x}_i$ *and* $\boldsymbol{x}_j$ are independent

$$\frac{\left(\dfrac{\partial V}{\partial \boldsymbol{x}_i}\right)_{p,T}}{\left(\dfrac{\partial S}{\partial \boldsymbol{x}_i}\right)_{p,T}} \neq \frac{\left(\dfrac{\partial V}{\partial \boldsymbol{x}_j}\right)_{p,T}}{\left(\dfrac{\partial S}{\partial \boldsymbol{x}_j}\right)_{p,T}}$$

hydrodynamic approximation

It is assumed that the large macrosystem can be divided to small subsystems. The size of each is small as compared to the whole system and large as compared to molecules (atoms) so that methods of statistics are applicable. This will be OK if the deviation of parameters a_i from the equilibrium values a_o are small. For instance the temperature change at distance l is small as compared to temperature itself.

$$\left| \frac{l}{a_i} \, grad a_i \right| << 1$$

Actually, this means that Gibbs equation is applicable in local form

$$Tds = du - pdv - \sum m_i dn_i$$

$$T \frac{ds}{dt} = \frac{du}{dt} - p \frac{dv}{dt} - \sum m_i \frac{dn_i}{dt}$$

The overall entropy in any moment is $S = \int sdv$

The usual procedure involves the equations of balance of mass and entropy (or energy)

If E is the local value of some extensive property

$$\frac{\partial E}{\partial t} = -div J_E + s_E$$

The conservation law means that the product of E inside the subsystem is not possible, i.e. $s_E = 0$ (E=mass, energy, etc.)

examples
For multicomponent closed system

$$\frac{\partial r_i}{\partial t} = -div J_{r_i} + s_{r_i}$$

In framework of Newtonian mechanics the conservation law claims

$$\sum s_{ri} = 0 \qquad \text{with } r = \sum r_i$$

$$\frac{\partial r}{\partial t} = -div J_r$$

where $J_r = \sum J_{ri} = \sum \boldsymbol{r}_i u_i$; u_i is the average speed of the ith component

$$J_i = \boldsymbol{r}_i(u_i - u_o) + \boldsymbol{r}_i u_o \qquad (*)$$

The average mass rate of the system is $u_o = \dfrac{\sum \boldsymbol{r}_i u_i}{\boldsymbol{r}}$

In (*) the second term accounts for the convective flux while the first term accounts for the diffusive flux.

Entropy balance

$$\frac{\partial s}{\partial t} = \sum \left(\frac{\partial s}{\partial \boldsymbol{r}_i} \right) \frac{\partial \boldsymbol{r}_i}{\partial t}$$

As soon as $\quad \dfrac{\partial s}{\partial \boldsymbol{r}_i} = -\dfrac{\boldsymbol{m}_i}{T} \quad \Rightarrow \quad \dfrac{\partial s}{\partial t} = -\sum \dfrac{\boldsymbol{m}_i}{T} \dfrac{\partial \boldsymbol{r}_i}{\partial t} \qquad (**)$

If a chemical reaction j is taking place at a rate (per unit volume) w_j with stoichiometric coefficient $\boldsymbol{n}_{ij}$ then from the balance of mass:

$$\boldsymbol{s}_{ri} = \sum \boldsymbol{n}_{ij} w_j$$

Therefore: $\qquad \dfrac{\partial \boldsymbol{r}_j}{\partial t} = -div J_j + \sum \boldsymbol{n}_{ij} w_j \quad$ With Eq.(**) this gives:

$$\frac{\partial s}{\partial t} = -\sum_i \sum_j \frac{\boldsymbol{m}_i}{T} \boldsymbol{n}_{ij} w_j + \sum_i \frac{\boldsymbol{m}_i}{T} div J_i =$$

$$= \sum_j \left[-\sum_i \frac{\boldsymbol{m}_i}{T} \boldsymbol{n}_{ij} \right] w_j + div \sum_i \frac{\boldsymbol{m}_i}{T} J_i - \sum J_i \nabla \frac{\boldsymbol{m}_i}{T}$$

The Affinity of the jth reaction

$$A_j = -\sum_j \boldsymbol{m}_i \boldsymbol{n}_{ij} \quad \text{it can be presented also as:} \quad A_j = kT \, ln \frac{K^{eq}(T.p)}{\prod_j r_j^{\boldsymbol{n}_{ij}}}$$

The equilibrium constant of reaction is: $\qquad K^{eq}(T, p) = \prod_j \boldsymbol{r}_{j,eq}^{\boldsymbol{n}_{ij}}$

At equilibrium $\quad A^{eq} = 0$. *It is seen that affinity is a measure of declination from equilibrium state. It play a role similar to $\tilde{\boldsymbol{N}}_{m\mu}$ in transport theory.*

$$\frac{\partial s}{\partial t} = \sum_j \frac{A}{T} w_j - \sum J_i \nabla \frac{m_i}{T} + div \sum_i \frac{m_i}{T} J_i$$

This expression can be considered as consisting of two terms:

$$\boldsymbol{s}_s \equiv \sum_j \frac{A}{T} w_j - \sum J_i \nabla \frac{m_i}{T}$$

and

$$divJ_s = div \sum_i \frac{m_i}{T} J_i$$

It is seen that $\boldsymbol{s}_s$ is a bilinear function of J_j and w_j (generalized fluxes) $\boldsymbol{J_k}$ related to nonreversible processes. It is as well a bilinear form of $\nabla \frac{m_i}{T}$ *and* $\frac{A_i}{T}$ that could be considered as generalized forces $\boldsymbol{X_k}$ causing the fluxes.

$$\boldsymbol{s} = \sum J_k X_k$$

$$\frac{\partial s}{\partial t} = \boldsymbol{s}_s - divJ_s$$

If we integrate the last equation over the volume, from the condition of mechanical equilibrium and the *div* rule:

$$\frac{\partial S}{\partial t} = \int \boldsymbol{s} dv_s - \int divJ_s dv = \int \boldsymbol{s} dv_s - \int_S \boldsymbol{n} J_s d\boldsymbol{S} \equiv \frac{\partial_e S}{\partial t} + \frac{\partial_i S}{\partial t}$$

Σ is the surface $\boldsymbol{n}$ is the unit vector

For isolated system the flux of entropy across the system is $\frac{\partial_e S}{\partial t} = 0$.

The II law of thermodynamics states $\frac{\partial_i S}{\partial t} \geq 0$

Therefore, $\boldsymbol{s}_S \geq 0$ when the method of local description is OK

PRIGOGINE RATIO

It is often useful to describe Affinity as:

$$A_i = -\left(\frac{\partial G}{\partial \boldsymbol{x_i}}\right)_{T,p,\boldsymbol{x_j}}$$

$$dG = -SdT + pdV - \sum_i A_i d\boldsymbol{x_i}$$

$$dG = -SdT + pdV - \sum A \, d\boldsymbol{x}$$

Mixed derivatives of a function of state are equal

$$\frac{\partial V}{\partial \boldsymbol{x}} = \frac{\partial^2 G}{\partial P \partial \boldsymbol{x}} = \frac{\partial^2 G}{\partial \boldsymbol{x} \partial P} = -\frac{\partial A}{\partial P}$$

compressibility

$$k = -\frac{1}{V_o}\left(\frac{\partial V}{\partial P}\right)_T \quad \Rightarrow \quad \Delta k = -\frac{1}{V_o}\left(\frac{\partial V}{\partial \boldsymbol{x}}\right)_T \frac{d\boldsymbol{x}}{dP} = -\frac{1}{V_o}\left(\frac{\partial^2 G}{\partial P \partial \boldsymbol{x}}\right)\frac{d\boldsymbol{x}}{dP}$$

heat capacity

$$c_p = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_p = T\left(\frac{\partial S}{\partial T}\right)_p \quad \Rightarrow \quad \Delta C_p = T\left(\frac{\partial S}{\partial \boldsymbol{x}}\right)_p \frac{d\boldsymbol{x}}{dT} = -T\left(\frac{\partial^2 G}{\partial T \partial \boldsymbol{x}}\right)\frac{d\boldsymbol{x}}{dT}$$

Thermal expansion coefficient

$$\boldsymbol{a} = \frac{1}{V_o}\left(\frac{\partial V}{\partial T}\right)_P \quad \Rightarrow$$

$$\Delta\boldsymbol{a} = \frac{1}{V_o}\left(\frac{\partial V}{\partial \boldsymbol{x}}\right)_P \frac{\partial \boldsymbol{x}}{\partial T} = \frac{1}{V_o}\left(\frac{\partial^2 G}{\partial P \partial \boldsymbol{x}}\right)\frac{\partial \boldsymbol{x}}{\partial T}$$

Therefore

$$\boxed{\frac{\Delta C_p \Delta k}{V_o T (\Delta \boldsymbol{a})^2} = 1}$$

Linear non-equilibrium thermodynamics
Equilibrium condition is:

1. All generalized forces X_k are zero (e.g. $A_j^{eq} = 0$ chem. equilibrium)
2. There are no fluxes ; $J_k = 0$

This gives good reason to assume that close to equilibrium all generalized forces X_k are weak and fluxes can be expressed as a Taylor series

$$J_k(X_l) = J_k(0) + \sum_l \left(\frac{\partial J_k}{\partial X_l}\right)_o X_l + \frac{1}{2}\sum_{l,m}\left(\frac{\partial^2 J_k}{\partial X_l \partial X_m}\right)_o X_l X_m + ...$$

As the first term is zero the truncated series gives:

$$J_k = \sum_l L_{kl} X_l \quad ; \quad L_{kl} = \left(\frac{\partial J_k}{\partial X_l}\right)_o$$

This equation, together with the expression for the balance of mass is a complete system that permits an exact calculation of generalized forces or of the thermodynamic variables.

Essential point is the Onzager equation:

$$L_{ik} = L_{ki}$$

Onzager determines two **dissipative** functions

$$\boldsymbol{j}(X,X) = \frac{1}{2}\sum_{1,k} L_{ik} X_i X_k \geq 0$$

$$\boldsymbol{F}(J,J) = \frac{1}{2}\sum_{i,k} L_{ik}^{-1} J_i J_k \geq 0$$

These two functions are measures for local irreversibility. In the framework of linear approximation $\boldsymbol{F} = \boldsymbol{j} = \frac{1}{2}\boldsymbol{s}$

It can be shown that these functions have behaviour of potentials

$$\frac{\partial \boldsymbol{j}}{\partial x_i} = \sum L_{ik} X_i = J_i$$

and

$$\frac{\partial^2 \boldsymbol{j}}{\partial X_i \partial X_k} = \frac{\partial J_i}{\partial X_k} = L_{ik} = L_{ki} = \frac{\partial J_k}{\partial X_i} = \frac{\partial^2 \boldsymbol{j}}{\partial X_k \partial X_i}$$

It follows that **j**, **F** and **s** are nonequilibrium potential functions

Prigogine Principle   Stationary state is a state characterized with minimal entropy production for the given external conditions.

In general – The nonequilibrium processes proceed in such a way that forces are not increasing. Generalizing to nonlinear case is: The processes proceed in a way thet entropy production is not increasing

E X A M P L E

Homogeneous multi-component system

$$\boldsymbol{s} = \sum_i w_i \frac{A}{T} \equiv \sum_i J \frac{A}{T}$$

According to the linear law:

$$\frac{d\boldsymbol{x}_i}{dt} = J_i = L_{ik} \frac{A_k}{T}$$

Near equilibrium

$$A \approx \frac{\partial A}{\partial \boldsymbol{x}} (\boldsymbol{x} - \boldsymbol{x}_e)$$

$$\frac{d\boldsymbol{x}}{dt} = \frac{L}{T} \frac{\partial A}{\partial \boldsymbol{x}} (\boldsymbol{x} - \boldsymbol{x}_e)$$

Solution is:

$$\boldsymbol{x} - \boldsymbol{x}_e = Ce^{-\frac{t}{t}}$$

The relaxation time is: $\boldsymbol{t} = -\dfrac{T}{L\left(\dfrac{\partial A}{\boldsymbol{x}}\right)}$

REM: Strictly speaking $w = \vec{w}\left[1 - exp\left(-\dfrac{A}{kT}\right)\right]$

Therefore linear approximation is valid for $\left|\dfrac{A}{kT}\right| \ll 1$

Concluding Remarks

We have seen that for isolated nonequilibrium systems $d_eS>0$. However, for open systems, it is possible to reach a stable stationary state corresponding to condition

$d_eS=-d_iS < 0$. This is to say that living organisms or society structures are possible if sufficiently large negative entropy fluxes flow through the systems.

Far from equilibrium, nonlinear systems of differential equations describe the processes. As there is no unique solution (unlike the linear case) of these systems, the Nature variety is guaranteed