Mechanics and Physics of Porous Solids

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Based on a lecture from O. Coussy and M. Vandamme





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- 2 Basics of thermodynamics and thermochemistry
- Basics of Mechanics
- The saturated porous solid
- 5 The unsaturated porous solid
- 6 Confined phase transitions
- Experimental considerations

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What is thermodynamics ?

Definition from the Collins English dictionnary

The branch of physical science concerned with the interrelationship and interconversion of different forms of energy and the behaviour of macroscopic systems in terms of certain basic quantities, such as pressure, temperature, etc.

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What will we cover with thermodynamics ?

- Ideal gas and mixtures
- Solution and solutes
- Raoult's and Henry's law
- Osmotic swelling
- Chemical reaction and equilibrium

Definition of a system



Open system: can exchange heat, work and matter with the outside

Closed system: can exchange heat and work with the outside

Isolated system: no exchange with the outside

Intensive and extensive variables

Intensive variables: The value does not change following a change of scale

- Temperature
- Pressure
- Chemical potential
- . . .

Extensive variables: The value is modified by the change of scale with the same ratio

- Entropy
- Volume
- Mole quantity

• . . .

Every intensive variable is associated to an extensive one. p/V, S/T, N/ μ ...

Oth law

For a system at equilibrium (every state variable are remaining constant), one can define a temperature T (intensive) which is homogeneous in the whole system

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3rd law

If a system approaches the absolute zero temperature, entropy reaches an absolute minimum value

1st law of thermodynamics

U the internal energy:

$\delta U = \delta Q + \delta W$

 δQ infinitesimal heat evolution, δW infinitesimal work evolution Internal energy encompasses all forms of energy i.e. potential energy, elastic energy, kinetic energy ...

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 δW is the sum of all the work exchanged

Especially, the work of external pressure: $\delta \textit{W}_{\textit{p}} = -\textit{p}_{\textit{ext}}\textit{dV}$



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The infinitesimal variation of internal energy for a system uniquely subjected to the work of pressure is then:

$$dU = -pdV + \delta Q$$

At constant volume, the variation of internal energy reduces to $dU = \delta Q$

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Legendre tranform

Legendre transform is defined for a function f as f(y) = g(x) - xy with y = g'(x)Allows to change the set of variable for a function. In thermodynamics, Legendre transform allows to exchange the place of an intensive variable and its associated extensive variable: p/V, T/S, μ/N ...

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Enthalpy

$$\begin{split} H &= U + pV \text{ (we have } \frac{\partial U}{\partial V} = -p \text{)} \\ dH &= \delta Q + V dp \\ \text{At constant pressure, the variation heat is stored in the enthalpy} \end{split}$$



Kamerlingh-Omnes

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Kamerlingh-Omnes

Internal energy is adapted when considering a problem where the volume is controlled. Enthalpy is adapted when considering a problem where the pressure is controlled

2nd law: entropy

Entropy

We postulate the existence of entropy S as the extensive variable which is linked to heat transfer. Heat transfer δQ can be written:

 $\delta Q \leq T dS$

T is the intensive variable associated to entropy There is equality when the process is non-dissipative (reversible). $TdS - \delta Q$ is the energy dissipated during the transformation.

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Dissipation and reversibility

A process is called reversible if there is no production of entropy \rightarrow we can rewind the movie

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Arrow of time

The second principle says that for whatever transformation of an isolated system: $\frac{dS}{dt} \geq 0$ The equality is valid for reversible processes Universe is an isolated subjected to an irreversible transformation \rightarrow the entropy of the Universe is ever increasing

Microscopic entropy: Boltzmann definition

In statistical thermodynamics, entropy is not a postulate

Entropy is defined as the measure of the number of possible microstates of a system in thermodynamic equilibrium, consistent with its macroscopic thermodynamic properties.

$$S = k_B \ln \Omega$$

 Ω is the number of microstates consistent with the observed macrostate. k_B is the Boltzmann constant.

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Entropy measures the lack of information

The higher the entropy the more microstates are possible. Because of thermal fluctuations the system is always changing of microstate even at equilibrium.



Boltzmann tomb

Thermodynamic potentials

dU = TdS - pdV (holds also for a non-reversible process as U is a state variable)

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Use of Legendre transform to change the set of variables

We define the Helmholtz free energy F and the Gibbs free energy G as: F = U - TSG = H - TS = U + PV - TS (also called free enthalpy)



Willard Gibbs



Hermann von Helmholtz

Importance and utility of the thermodynamical potentials

Helmoltz free energy

Let us consider a system subjected to an irreversible transformation.

 $dF = d(U - TS) \le -SdT + \delta W$

For an infinitesimal reversible isothermal transformation, $dF = \delta W$ The Helmholtz free energy is equal to the work obtained during the transformation. If no work is exchanged (V = cte) $dF \leq 0$

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Gibbs free energy

Let us consider a system whose T and p are controlled.

 $dG = d(H - TS) \le -SdT + Vdp = 0$

G always decreases and reaches a minimum at equilibrium

Partial molar quantities

Mixture of ethanol and water

- 1 mol of water in 1L of water \Rightarrow volume increase of 18 cm³
- 1 mol of water in 1L of ethanol \Rightarrow volume increase of 14 cm³

The identity of the surrounding molecules modifies the volume increase



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Euler Theorem

Let us consider an extensive property $Z(T, p, n_i)$ (such as volume, enthalpy...)

As Z is extensive: $Z(T, p, \lambda n_i) = \lambda Z(T, p, n_i)$ (change of scale)

$$Z(T, p, n_i) = \sum_i n_i \overline{Z}_i$$
 with $Z_i = \left(rac{\partial Z}{\partial n_i}
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In the case of water and ethanol, $\bar{V}_w = \frac{\partial V}{\partial n_w} < v_w$, with v_w the pure molar volume of water

Chemical potential

Exchange of matter in an open system

Let us define the intensive variable μ_i associated with the extensive variable n_i , the mole quantity of species *i* in the system.

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The different thermodynamic potentials are then rewritten (reversible infinitesimal transformation)

- $dU = TdS pdV + \sum_i \mu_i dn_i$
- $dH = TdS + Vdp + \sum_{i} \mu_{i} dn_{i}$
- $dF = -SdT pdV + \sum_i \mu_i dn_i$
- $dG = Vdp SdT + \sum_i \mu_i dn_i$

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$$dF = -SdT - pdV + \sum_{i} \mu_{i} dn_{i}$$

• $dG = Vdp - SdT + \sum_i \mu_i dn_i$

And the chemical potential verifies then the following equations

$$\mu_{i} = \left(\frac{\partial U}{\partial n_{i}}\right)_{S,V,n_{j\neq i}} = \left(\frac{\partial H}{\partial n_{i}}\right)_{S,p,n_{j\neq i}} = \left(\frac{\partial F}{\partial n_{i}}\right)_{T,V,n_{j\neq i}} = \left(\frac{\partial G}{\partial n_{i}}\right)_{T,p,n_{j\neq i}} = \bar{G}_{i}$$

Gibbs-Duhem equation

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Gibbs-Duhem relation

$$dG = Vdp - SdT + \sum_{i} \mu_{i} dn_{i} = \sum_{i} n_{i} d\mu_{i} + \sum_{i} \mu_{i} dn_{i}$$

$$\Rightarrow SdT - Vdp + \sum_{i} n_{i} d\mu_{i} = 0$$

For a system at constant temperature and pressure GD relation simplifies to $\sum_i n_i d\mu_i = 0$

Chemical equilibrium

Let's consider a closed system with 1 constituents divided in 2 phases J and K at a constant ${\cal T}$ and p

$$dG = \mu^J dn^J + \mu^K dn^K = \left(\mu^K - \mu^J
ight) dn^{J
ightarrow K} \leq 0$$

We reach equilibrium when dG = 0 i.e. $\mu^{K} = \mu^{J}$. The chemical equilibrium implies the equality of the chemical potential in all the phases (but DOES NOT imply the equality of the chemical potential of different species)



Equation for a pure perfect gas

pV = nRT

Maxwell relation gives: $\frac{\partial^2 G}{\partial n \partial p} = \frac{\partial^2 G}{\partial p \partial n} \implies \frac{\partial \mu}{\partial p} = \frac{\partial V}{\partial n} = \frac{RT}{p}$ After integration we obtain: $\mu(p, T) = \mu^0(T) + RT \ln(p/p^0)$

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We keep the same relation but we use the fugacity $f = \Phi p$ instead of p

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For a mixture, the pressure (or fugacity) is replaced by the partial pressure of the gas: $p_i = x_i p_{tot}$ with $x_i = \frac{n_i}{\sum_i n_i}$ the molar fraction (Dalton)

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The reference state μ^0 is taken by convention as the pure perfect gas at p = 1 bar.

Chemical potential of solutions

By analogy with the perfect gas, we define the chemical potential of a solution as a sum of a standard chemical potential and a activity term:

$$\mu_i = \underbrace{\mu_i^0}_{i} + \underbrace{RT \ln a_i}_{i}$$

standard state

activity term

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$$\mu_i = \underbrace{\mu_i^0}_{\text{standard state}} + \underbrace{RT \ln a_i}_{\text{activity term}}$$

According to the situation,3 definitions of activity are possible:

•
$$a_i = \gamma_i^1 x_i$$
 molar fraction $x_i = \frac{n_i}{\sum_i n_i}$
• $a_i = \gamma_i^2 c_i$ molar concentration $c_i = \frac{n_i}{\frac{n_i}{V_{\text{solution}}}}$
• $a_i = \gamma_i^3 m_i$ molality $m_i = \frac{n_i}{\frac{n_i}{M_{\text{solvent}}}}$

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| • | $a_i = \gamma_i^2 c_i$ | molar concentration | $c_i = \frac{\sum_{i=1}^{j}}{V_{\text{solution}}}$ |
| • | $a_i = \gamma_i^3 m_i$ | molality | $m_i = \frac{n_i}{M_{\text{solvent}}}$ |

The standard state of a solute is defined as:

1 mole of the considered species in an hypothetical solution behaving as infinitely diluted containing 1kg of water for any temperature and pressure Helgeson *et al.* 1981



Mixing of 2 gases at temperature and pressure constant

$$\Delta G = n_1 \mu_1 + n_2 \mu_2 - (n_1 \mu_1^0 + n_2 \mu_2^0)$$

$$\Delta G = RTn_1 \ln (x_1 \Phi_1 / \Phi_1^0) + RTn_2 \ln (x_2 \Phi_2 / \Phi_2^0)$$



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Composition and excess Gibbs free energy of mixing

$$\Delta G = \underbrace{RT \sum_{i} n_{i} \ln x_{i}}_{\text{composition}} + \underbrace{RT \sum_{i} n_{i} \ln \Phi_{i} / \Phi_{i}^{0}}_{\text{excess}}$$



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Gibbs free energy of mixing is always negative: mixing is a spontaneous process (no reversibility)

Entropy of mixing

$$\Delta S = \left(\frac{\partial \Delta G}{\partial T}\right)_{p,n_i} = \underbrace{-R \sum_{i} n_i \ln(x_i)}_{S^{comp}} - \underbrace{\left(R \sum_{i} n_i \ln \Phi_i / \Phi_i^0 + RT \sum_{i} n_i \left(\frac{\partial \Phi_i / \Phi_i^0}{\partial T}\right)_{p,n_i}\right)}_{S^{ex}}$$

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- Creation of entropy during the mixing: we are increasing the number of possible microstates
- Excess entropy measures the difference of interaction between the molecules which can decrease of increase the global entropy of mixing
- For an ideal mixing, the enthalpy is zero: no heat exchanged.

Application of chemical potentials Raoult's law

What is the equilibrium partial pressure of vapor above a liquid mixture ? Example of *J* component:

- Chemical potential of the vapor: $\mu_J^v(p_J, T) = \mu_J^0(T) + RT \ln(p_J/p^0)$
- Chemical potential of the solvent: $\mu'_J(p, T) = \mu^*_J(p, T) + RT \ln x_J$

The thermodynamic equilibrium gives: $\mu_J^0(T) + RT \ln(p_J/p^0) = \mu_J^*(p, T) + RT \ln x_J$ In the case of a pure component, $x_J = 1$ and then $\mu_J^0(T) - \mu_J^*(p, T) = RT \ln(p_J^*/p_J)$

Raoult law

The partial pressure of component J over a mixture is equal to $p_J = x_J p_J^*$, with p_J^* the partial pressure over the pure component



Application of chemical potentials Henry's law

Case of a solution: what is the concentration of a gas in a solution ?

Thermodynamic equilibrium : $\mu_J^0(T) + RT \ln(p_J/p^0) = \mu_J^*(p, T) + RT \ln x_J$

Can be rewritten
$$p_J = x_J \times \underbrace{p^0 \exp\left(\frac{\mu_J^*(p, T) - \mu_J^0(T)}{RT}\right)}_{\kappa_H(p, T)}$$

with $K_H(T)$ the Henry constant. $K_H(298.15\text{K},\text{N}_2) = 9.077.10^4$ atm

- Decompression stages for divers
- Beer foam when opening the bottle
- Dissolution of CO₂ in the oceans



Application of chemical potentials Osmostic swelling

Two containers separated by a membrane permeable to solvent but not solute

- chemical potential of the pure solvent: $\mu^*(p, T)$
- chemical potential of the solution: $\mu^*(p + \Delta p) + RT \ln(1 x)$

Taylor development (for infinitely diluted solutions) and thermodynamical equilibrium: $\Delta p \frac{\partial \mu^*}{\partial p} = RT_X$

 $\Delta p = \frac{RT}{v} = RTc$ v being the molar volume of the solution

- Migration of the solvent to the solution to equalize the concentrations
- Reverse osmosis to purify water



Let us consider a the following chemical reaction $A_{\nu_A}B_{\nu_B}\ldots=\nu_AA+\nu_BB\ldots$ The molar quantity of reaction for an extensive property is:

$$\Delta_r X = \sum_i \nu_i \left(\frac{\partial X}{\partial n_i} \right)_{T, p, n_{i \neq j}}$$

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Gibbs free energy of reaction

$$\Delta_{r}G = \sum_{i} \nu_{i} \left(\frac{\partial G}{\partial n_{i}}\right)_{T,p,n_{i\neq j}} = \sum_{i} \nu_{i}\mu_{i}$$
$$\Delta_{r}G = \sum_{i} \nu_{i}^{0} + \sum_{i} RT \ln a_{i}$$
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$$\Delta_{r}G = \Delta_{r}G^{0} + RT \ln Q_{r}$$

- $\Delta_r G^0(p, T) \Rightarrow$ standard Gibbs free energy of reaction
- $Q_r \Rightarrow$ lon activity product (or reaction quotient)

1

Extent of reaction (De Donder Variable)

$$d\xi = \frac{dn_i}{\nu_i}$$

For example CaCl₂ = $Ca^{2+} + 2Cl^-$
 $d\xi = -dn_{CaCl_2} = dn_{Ca^{2+}} = dn_{Cl_-}/2$

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Equilibrium

The Gibbs free energy is decreasing for a system at constant ${\cal T}$ and p. At equilibrium $\frac{dG}{d\xi}=0$

 $dG = \sum_{i} \mu_{i} dn_{i} = \sum_{i} \mu_{i} \nu_{i} d\xi = \Delta_{r} G d\xi$

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The Gibbs free energy is decreasing for a system at constant ${\cal T}$ and p. At equilibrium $\frac{dG}{d\xi}=0$

$$dG = \sum_{i} \mu_{i} dn_{i} = \sum_{i} \mu_{i} \nu_{i} d\xi = \Delta_{r} G d\xi$$

At equilibrium $\Delta_r G = 0$

We define the equilibrium constant as $\Delta_r G^0 = -RT \ln K_s$ At equilibrium, $Q_r = K_s \Rightarrow K_s = \prod_i a_i^{\nu_i}$ Mass action law

Example: Swellling of bentonite in water

Bentonite is a kind of clay (mostly Montmorillonite $(Na,Ca)_{0.33}(AI,Mg)_2(Si_4O_{10})(OH_2) \cdot nH_2O)$ which swells strongly in water)

Bentonite is composed of small platelets (size Å) with a negative surface charge q. The solution is charged with ions (concentrations c_+ and c_-). Two platelets are separated with a distance 2d. The concentration of the solution outside the bentonite is c_{∞}





Example: swelling of bentonite in water

Electroneutrality:
$$2q + \int_{-d}^{+d} F(c_{+}(x) + c_{-}(x)) dx = 0$$

Electrostatic pressure on the platelets: $p_{el} = \frac{q^2}{2\varepsilon_0\varepsilon_r} + \frac{q}{2\varepsilon_r\varepsilon_0} \int_{-d}^{+d} F(c_{+}(x) - c_{-}(x)) dx = -\frac{q^2}{2\varepsilon_0\varepsilon}$
Excess pressure on the platelets: $p_{tot} = \underbrace{RT[c_{+}(d) + c_{-}(d) - 2c_{\infty}]}_{\text{osmotic pressure}} + p_{el}$

$$\begin{cases} \text{Chemical potential of the cations:} & \mu_{+}(x) = \mu_{+}^0(x) + RT \ln c_{+}(x) + F\psi(x) \\ \text{Chemical potential of the anions:} & \mu_{-}(x) = \mu_{-}^0(x) + RT \ln c_{-}(x) - F\psi(x) \end{cases}$$

$$\begin{cases} \mu_{+}(x) = \mu_{+}(\infty) \\ \mu_{-}(x) = \mu_{-}(\infty) \end{cases} \Rightarrow \begin{cases} RT \ln c_{+}(x) + F\psi(x) = RT \ln c_{\infty} \\ RT \ln c_{-}(x) - F\psi(x) = RT \ln c_{\infty} \end{cases} \Rightarrow \begin{cases} c_{+}(x)c_{-}(x) = c_{\infty}^{2} \\ c_{x}(x) = c_{\infty} \exp\left(-F\psi/RT\right) \\ c_{x}(x) = c_{\infty} \exp\left(F\psi/RT\right) \end{cases}$$

Example: swelling of bentonite in water

Poisson equation between the platelets: $\Delta \psi = -\frac{F}{\varepsilon_0 \varepsilon_r} [c_+(x) - c_-(x)]$

Using electroneutrality and symmetry $\frac{d\psi}{dx}\Big|_{x=0} = 0$ we obtain $\frac{d\psi}{dx}\Big|_{x=d} = \frac{q}{\varepsilon_0\varepsilon_r}$

Combining the expressions of c_+ and c_- with the Poisson equation, we obtain after integration $\frac{1}{2}\varepsilon_0\varepsilon_r\left(\frac{d\psi}{dx}\right)^2 = RT\left[c_+(x) + c_-(x) - c_+(0) - c_-(0)\right]$

Combining the last equations with the expression of pressure we get: $p_{tot} = RT [c_+(0) + c_-(0) - 2c_\infty]$ which is always positive: repulsion

Finally, considering the Poisson equation, the characteristic length of the system is $L = \sqrt{\frac{\varepsilon_0 \varepsilon_r RT}{2c_{\infty} F^2}}$ (Debye Length)

The characteristic distance between two platelets is inversely proportional to the squareroot of the outside concentration. Bentonite swells less with salted water than with pure water because of the osmotic pressure

Mainly used for sealing purposes in civil engineering especially in the radioactive waste repositories.



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